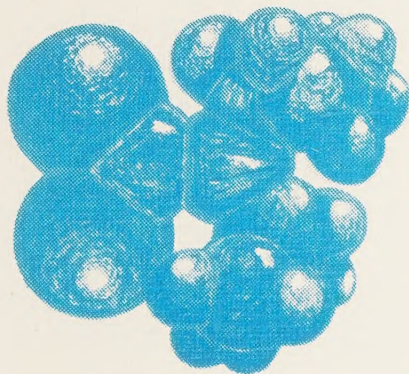


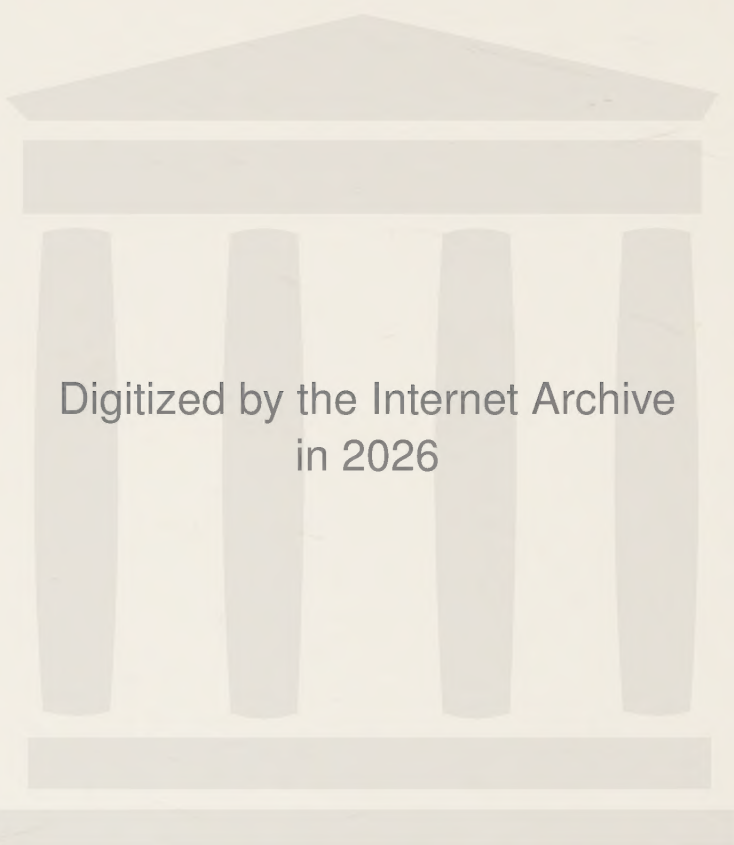
**ON STERIC EFFECTS
IN SOLID
DITHIOCARBAMATE
COMPOUNDS**

by

Ingvar Ymén



Lund 1983



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ON STERIC EFFECTS IN SOLID
DITHIOCARBAMATE COMPOUNDS

AVHANDLING FÖR FILOSOFIE DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid offentlig disputation
å Kemicentrum, hörsal D, fredagen den 29 april kl. 10.15.

av
Ingvar Ymén
Fil.kand., Hld

**ON STERIC EFFECTS
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Lund 1983

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DOKUMENTTITEL OCH UNDERTITEL ON STERIC EFFECTS IN SOLID DITHIOCARBAMATE COMPOUNDS			
SAMMANFATTNING The crystal structures of some Li^+- and Na^+-dithiocarbamate compounds, one tris(dithiocarbamato)iron(III) compound and two thiuramdisulfides have been studied. All structures were determined with <u>X-ray diffraction techniques</u>. One of the compounds was also studied with <u>neutron diffraction</u> and four with ESCA. It is shown that there is a strong correlation between the <u>ligand bite</u> and the bulkiness of the substituents R in $-\text{S}_2\text{CNR}_2$. The ligand bite decreases as the substituents become bulkier in the series $R_2=(\text{CH}_2)_4$, $(\text{CH}_3)_2 \sim (\text{C}_2\text{H}_5)_2$, $(\text{CH}(\text{CH}_3)_2)_2$. This is interpreted as the result of <u>increasing steric intramolecular interference</u>, C-H...S, in the series given above. From ESCA measurements it is concluded that <u>small ligand bites</u> are associated with <u>smaller charges</u> on the S-atoms than larger ones. The result is used to propose a model for the influence of the substituents, R, on the magnetic properties of tris(dithiocarbamato)iron(III) compounds. The model suggests that <u>strong steric interference</u> results in <u>small ligand bites</u> and <u>strong ligand fields</u>, causing <u>low-spin</u> compounds. <u>Weak steric interference</u> results in <u>large ligand bites</u> and <u>weak fields</u>. The corresponding compounds will be <u>high-spin</u>. <u>Intermediate steric interference</u> produces <u>intermediate fields</u> and <u>cross-over behaviour</u>.			
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ABBREVIATIONS

dtc = Dithiocarbamate i.e. $\text{S}_2\text{CNRR}'$

tds = Thiuram disulfide i.e. $[\text{S}_2\text{CNRR}']_2$

HS = High spin

LS = Low spin

CO = Cross over

INTRODUCTION

A research programme at this Institute aims at correlating the magnetic behaviour of various substituted tris(dithiocarbamato)iron(III) complexes, $\text{Fe}(\text{S}_2\text{CNRR}')_3$, with geometric features such as the FeS_6 polyhedron, the $\text{S}_2\text{CNRR}'$ -group and the packing of the complexes.

The aim of this investigation is to elucidate the effects of different substituents, R, on the geometry of the S_2CNC_2 -moiety and to propose a model for the influence of the substituents on the magnetic behaviour of solid tris(dithiocarbamato)iron(III) derivatives. For this purpose the crystal structures of some solid alkali-metal dithiocarbamate compounds, one tris(dithiocarbamato)iron(III) compound and two thiuram disulfides have been studied. All structures were determined using single-crystal X-ray techniques. One of the compounds has also been studied by neutron diffraction and four with ESCA (Electron Spectroscopy for Chemical Analysis). The results have been reported in the following papers:

The Structure of Sodium 1-Pyrrolidinecarbodithioate Dihydrate at 295, 150 and 27 K: A Study of Conformational Reorientation¹

X-ray Study of Tris(N,N-dimethyldithiocarbamato)iron(III) at the two Extreme Temperatures 25 and 400 K²

Neutron Diffraction Study of Sodium 1-Pyrrolidinecarbodithioate Dihydrate³

Crystal Structure of Sodium Dimethyldithiocarbamate Dihydrate⁴

Structure of Lithium 1-Pyrrolidinecarbodithioate Tetrahydrate⁵

Crystal Structures of N,N,N',N'-bis-(tetramethylene)thiuram Disulfide and Tetramethylthiuram Disulfide⁶

Crystal Structure of Sodium Diisopropyldithiocarbamate Pentahydrate⁷

Influence of the Substituents on the Magnetic Properties of Tris-(dithiocarbamato)iron(III) compounds⁸

Crystal Structure of Lithium Dimethyldithiocarbamate Tetrahydrate⁹

Crystal Structure of Lithium Diisopropyldithiocarbamate Trihydrate¹⁰

Crystal Structure of Lithium Diethyldithiocarbamate Trihydrate¹¹

A part of this work has been carried out in collaboration with Dr Kenny Ståhl, who has studied the magnetic and structural properties of various tris(dithiocarbamato)iron(III) compounds in a parallel investigation.¹²

Dithiocarbamate ions, $^{-}S_2CNRR'$ (dtc), form compounds with a large variety of metal ions.¹³⁻¹⁵ They have the property of stabilizing metal ions in high oxidation states (e.g. Cu^{III} and Fe^{IV}),^{13,16-17} and usually form complexes of very high stability.¹³ There are a vast number of practical applications for dithiocarbamate compounds such as accelerators for the vulcanization of rubber,¹⁸⁻²⁰ additives in lubricating greases,²¹ fungicides and pesticides²²⁻²³ and corrosion inhibitors.²⁴ Their ability to form many stable complexes is used in analytical chemistry.²⁵⁻³¹ They have also been proposed as complexing agents for toxic metal ions in humans.³²

Much interest has been focused on the tris(dithiocarbamato)iron(III) compounds, $Fe(dtc)_3$.^{13-15,39} These compounds have magnetic properties which are strongly temperature dependent.³³⁻⁴³

In an octahedral field, the five degenerate d-orbital energy levels of the d^5 ion Fe^{3+} are split up in two levels, t_{2g} and e_g (Fig. 1).

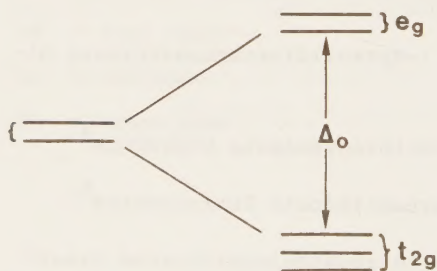


Fig.1

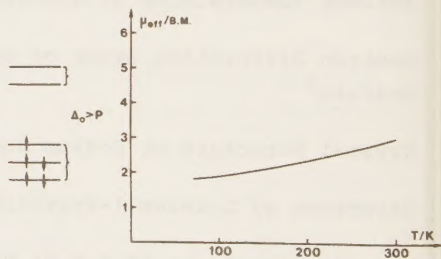


Fig.2a

The magnitude of the ligand field splitting, Δ_o , is dependent on the set of ligands. If $\Delta_o > P$ (the average spin pairing energy) the five d-electrons will enter the t_{2g} orbitals (Fig. 2a), leaving one unpaired electron. For such "low-spin" (LS) paramagnetic compounds the effective magnetic moment, μ_{eff} , is characteristically ~ 2.1 B.M.

If $\Delta_o < P$ the system will gain energy by having all five electrons unpaired (Fig. 2b) rendering a "high-spin" (HS) compound with $\mu_{eff} = \sqrt{35}$ B.M.

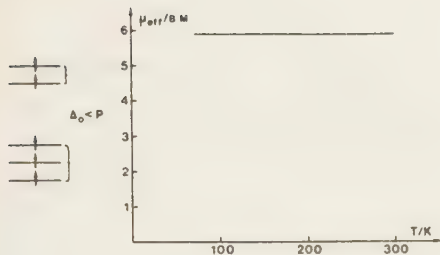


Fig.2b

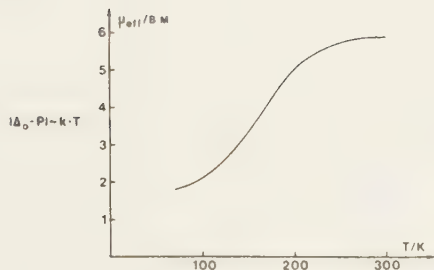
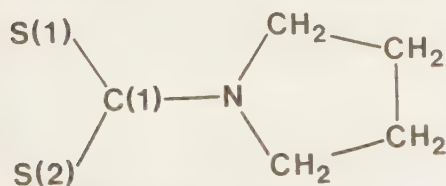


Fig.2c

When $\Delta_0 \sim P$ the absolute value of $\Delta_0 - P$ may become comparable to $k_B \cdot T$. As a result both the HS and LS states may be populated and co-exist in thermal equilibrium. This is referred to as "spin-crossover" (CO) i.e. μ_{eff} is strongly temperature dependent (Fig. 2c). For compounds $\text{Fe}(\text{S}_2\text{CNR}'')_3$ all three cases may be found both in solution and in the solid state.³⁸ The magnetic behaviour is dependent on the substituents R and R' and in some cases, in the solid state, on solvate molecules. The most obvious ways in which the substituents may influence the magnetic behaviour are inductive effects, cooperative effects and steric interference with the FeS_6 -core, i.e. steric interference with the S_2CNC_2 -moiety.



Tetremethylenedithiocarbamate

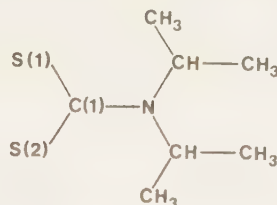
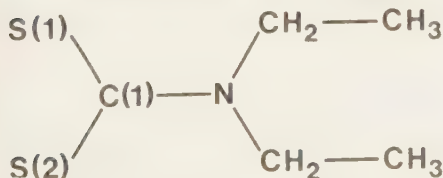
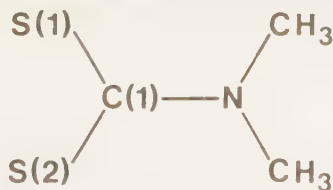


Fig.3

Diisopropyldithiocarbamate



Diethyldithiocarbamate



Dimethyldithiocarbamate

The four ligands shown in Fig. 3 were chosen for the present study since $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_2)_4)_3$ is a HS compound, $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_2)_2$ and $\text{Fe}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ exhibit CO behaviour and $\text{Fe}(\text{S}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2)_3$ is essentially LS. The iron compounds themselves are not the best choice for this investigation since the comparatively strong metal-ligand bonds influence the geometry of the dithiocarbamate ion. Furthermore

the crystal structures of CO Fe(III)dtcS contain a distribution of HS and LS units and the observed structures are averages of the HS and LS forms.¹² Therefore only one Fe(III)dtc has been studied. In order to be as close as possible to the pure HS and LS forms, it has been investigated at extreme temperatures. Instead the crystal structures of a number of Li⁺ and Na⁺-dtcS have been determined since the metal-ligand interactions are expected to be small in these compounds and the geometry observed may be approximated to that of an uncoordinated ("free") ligand. Since X-ray methods are used in all studies but one, another advantage of using these metal ions is their small scattering power, which allows the structural parameters for the light atoms in the dtc-ion to be determined very accurately.

Steric interference with the S₂CNC₂-moiety should result in a redistribution of the electron density, i.e. the charges on the atoms. The ESCA technique was chosen in order to determine any difference in charge distribution between the investigated dtc-ions.

The investigated alkali-dtcS are all hydrates with hydrogen bonds O...H-O and S...H-O. The O...H-O bonds in crystal hydrates has been extensively studied.⁴⁴⁻⁴⁶ However, hydrogen bonds S...H-O, which are also of biological interest,⁴⁷ are not so well characterized.⁴⁸ A short account of their geometry (as observed in the present structures) is given.

The coordination of Li⁺ and Na⁺ in inorganic and organic systems has been the subject of many studies.⁴⁹⁻⁵² Since Na-S and Li-S coordination has been rarely studied, the coordination situation in the investigated structures is briefly discussed.

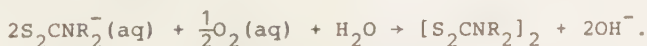
EXPERIMENTAL

Denotations of the investigated compounds are given in Table 1.

Preparations

$\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$ and $\text{LiS}_2\text{CN}(\text{CH}_2)_4 \cdot 4\text{H}_2\text{O}$ were obtained by evaporating solutions of $\text{NH}_4\text{S}_2\text{CN}(\text{CH}_2)_4$ in alkali hydroxide under reduced pressure at room temperature. The other alkali dtcs were prepared according to Uhlin & Åkerström.⁵³ Stoichiometric amounts of HNR_2 (in water or ethanol), CS_2 and $\text{MOH}(\text{aq})$ were mixed and stirred for 1-2 hours at 0°C . Evaporation under reduced pressure at room temperature yielded good single crystals, except for $\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$ and $\text{LiS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$, where temperatures less than 5°C were needed. All crystals decompose when removed from their mother liquid. The stability increases in the series $\text{III}, \text{VII} < \text{IV}, \text{V} < \text{I}, \text{II}$. Crystals of compound VI "melt" in moist air but are otherwise as stable as compounds IV and V. Single crystals of compounds belonging to the beginning of the above series are completely destroyed within minutes, those in the middle within a few days, while those at the end are stable for a couple of weeks. Since the crystals are much more stable when stored in closed vessels, some of these compounds were mounted in a glass capillary and coated with apiezon grease for the data collections. $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_2)_3$ was synthesized as described by Albertsson & Oskarsson.⁵⁴

In all syntheses hydrophobic contaminations were formed. The yield of the by-products was increased if air was bubbled through the solutions. Two of the by-products were determined (structurally) to be $[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ and $[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$. A probable reaction is



An acidic solution does not improve the yield in the synthesis of dtcs due to the decomposition of the free acid according to



X-ray crystallographic work

Cell dimensions for all compounds were calculated from accurate θ -values determined on a computer controlled Enraf-Nonius CAD4 four-

circle single-crystal diffractometer. Crystal data for the investigated compounds are given in Table 1.

Table 2 gives information concerning the data collection, data reductions and the least-squares refinements. The X-ray data for all compounds were collected with the CAD4 and the neutron data with a Hilger & Watts computer controlled four-circle diffractometer at the Swedish Atomic Energy reactor R2, Studsvik. A gas-stream apparatus working with liquid nitrogen (100-295 K)⁵⁶ and a Be-walled conduction-cooling He(l)-cryostat (15-50 K)⁵⁸ were used for the low-temperature work.

In order to be able to collect the data at 400 K for $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_2)_3$ a microfurnace had to be constructed (Fig. 4). The microfurnace and its temperature regulator unit is similar to that described by Lissalde, Abrahams & Bernstein.⁵⁷ To improve the mechanical stability and to allow water cooling between the furnace and the ϕ -axis shaft of the goniostat, the furnace was mounted on the same type of x,y,z-adjustments as is used on the liquid He-cryostat.⁵⁸ The furnace is operable from room temperature up to about 600 K. The long term stability at 400 K is better than ± 1 K.

Fig.4

A microfurnace for the CAD-4 diffractometer.

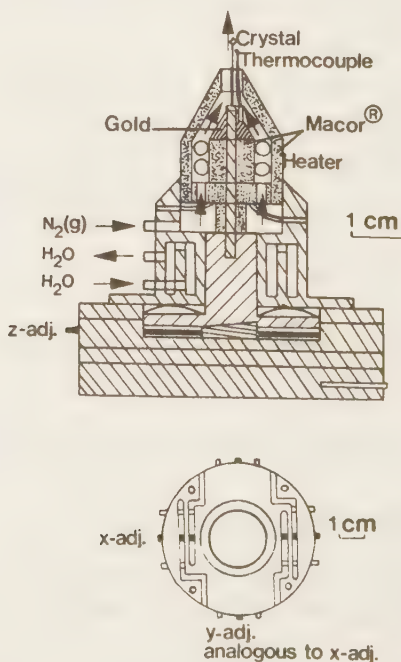


Table 1. Crystal data

		D/Mg·m ⁻³	Space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/Å ³	Z
I	NaS ₂ CN(CH ₃) ₄ ·2H ₂ O	1.407	P2 ₁ /a	12.121(4)	5.789(1)	14.008(2)	90	.. 98.58(2)	90	972(1)	4
I	"	1.423	"	12.050(4)	5.767(2)	13.937(5)	90	98.41(3)	90	958(1)	4
I	"	1.449	"	11.938(22)	5.716(6)	13.893(48)	90	98.56(25)	90	938(1)	4
II	NaS ₂ CN(CH ₃) ₂ ·2H ₂ O	1.434	"	11.981(1)	5.871(2)	12.878(1)	90	113.62(1)	90	830(1)	4
III	NaS ₂ CN(CH(CH ₃) ₂) ₂ ·5H ₂ O	1.243	"	5.983(1)	7.741(2)	17.545(1)	92.02(1)	94.73(1)	106.97(3)	773(6)	2
IV	LiS ₂ CN(CH ₂) ₄ ·4H ₂ O	1.292	P2 ₁ /n	10.279(1)	9.989(3)	11.291(1)	90	93.03(1)	90	1158(1)	4
V	LiS ₂ CN(CH ₃) ₂ ·4H ₂ O	1.281	P4 ₃	8.227(1)	8.227(1)	15.260(2)	90	90	90	1033.0(2)	4
VI	LiS ₂ CN(C ₂ H ₅) ₂ ·3H ₂ O	1.267	P $\bar{1}$	7.710(1)	8.784(3)	9.154(1)	77.88(1)	82.67(1)	64.93(2)	548.5(3)	2
VII	LiS ₂ CN(CH(CH ₃) ₂) ₂ ·3H ₂ O	1.215	P $\bar{1}$	6.143(1)	8.488(1)	12.796(1)	95.71(1)	101.32(1)	93.73(1)	648.5(1)	2
VIII	(S ₂ CN(CH ₂) ₄) ₂	1.436	A2/a	9.432(1)	10.432(1)	13.851(1)	90	97.08(1)	90	1353(1)	8
IX	(S ₂ CN(CH ₃) ₂) ₂	1.426	C2/c	9.672(1)	9.931(2)	11.882(8)	90	99.43(3)	90	1120(5)	8
X	Fe(S ₂ CN(CH ₃) ₂) ₃ , 25 K	1.604	Pbca	17.288(50)	19.947(26)	9.998(13)	90	90	90	3348(30)	8
X	"	1.480	"	17.696(1)	20.791(1)	10.163(1)	90	90	90	3739(6)	8

Table 2. Data collection, data reduction and refinements.

Compound	I 295K	I 150K	I 27K	I Neutrons	II	III
Crystal size (mm)	0.19x0.38 x0.07	0.33x0.44 x0.06	0.14x0.26 x0.07 0.38x0.24 x0.09	4.5x8.6 x0.7	0.09x0.50 x0.19	0.24x0.1 x0.04
$\lambda(\text{\AA})$	1.5418	0.71069	0.71069	1.210	0.71069	0.71069
Max. $\sin\theta/\lambda$ ($\text{\AA}^{-1}$)	0.61	1.00	1.08	0.63	0.70	0.70
Filter/ Monochromator	F	F	F	M	F	M
Scan type	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
Scan width, $\Delta\omega(^{\circ})$	0.9+0.4tan θ	0.9+0.5tan θ	1.0+tan θ	1.6	0.8+0.3tan θ	0.7+0.5tan θ
Max. recording time (s)	180	180	120	600	180	120
$\sigma(I)/I$ re- quested in a scan	0.028	0.028	0.030	stepscan 0.04 $^{\circ}$ /step	0.028	0.030
$\mu(\text{mm}^{-1})$	4.9	0.54	0.55	0.26(1)	0.61	0.37
Range of trans- mission factors	0.32-0.73	0.82-0.96	0.91-0.96	0.36-0.83	0.90-0.95	0.94-0.96
Number of re- flections in final LS cycles,m	1522	2237	1461	1132	1478	1187
Number of re- flections with zero weight	392	1700	1698	799	sorted	3397
Number of para- meters refined,n	138	137	138	210	122	218
m/n	11.0	16.3	10.6	5.4	12.1	5.4
R	0.031	0.050	0.056	0.069	0.034	0.053
R_w	0.033	0.052	0.066	0.082	0.038	0.064
S	0.72	0.89	0.99	0.84	0.94	0.96
$g \cdot 10^{-4}$ (extinction)	0.08(2)	-	-	0.36(10)	-	-

IV	V	VI	VII	X 400K	X 25K	VIII	IX
0.53x0.30 0.35	0.16x0.20 x0.44	-	0.44x0.10 x0.02	0.12x0.25 x0.32	0.06x0.28 x0.36 0.12x0.25 x0.32 0.06x0.32 x0.30	0.21x0.19 x0.19	0.50x0.20 x0.30
0.71069	0.71069	0.71069	1.5418	1.5418	1.5418 1.5418 0.71069	1.5418	0.71069
0.70	0.70	0.70	0.70	0.61	0.46 0.46 1.01	0.61	0.70
M	M	M	M	F	F	M	M
ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω	ω-2θ	ω-2θ
0.7+0.5tanθ	0.7+0.5tanθ	1.0+0.5tanθ	1.0+0.5tanθ	0.7+0.5tanθ	1.0+0.3tanθ 1.0+0.3tanθ 0.8+0.5tanθ	0.8+0.5tanθ	0.8+0.6tanθ
120	120	120	180	180	120	120	180
0.010	0.030	0.033	0.010	0.020	0.030 0.030 0.025	0.030	0.030
0.43	0.48	-	3.4	12.51	13.52 1.52	6.0	0.77
0.83-0.87	0.88-0.93	-	0.69-0.93	0.08-0.32	0.08-0.36 0.05-0.23 0.74-0.91	0.35-0.49	0.74-0.84
1680	1970	2573	920	1295	1737	1081	883
46	sorted	542	504	2684	712	368	903
84	151	174	209	173	229	106	80
4.6	13.0	14.8	4.4	7.5	7.6	10.2	11.0
0.030	0.037	0.041	0.047	0.058	0.046	0.041	0.041
0.041	0.038	0.056	0.057	0.065	0.061	0.061	0.053
0.89	1.19	1.59	1.00	1.07	1.10	1.43	0.91
0.9(1)	-	-	0.7(2)	0.24(6)	-	0.63(8)	0.29(8)

A number of standard reflections (usually 3 or 4) were measured at regular intervals during the data collections. For compounds I and II the peak analysis method of Lehmann & Larsen⁵⁹ was used to calculate $\underline{I}$ and $\sigma_c(\underline{I})$. Otherwise, $\underline{I}$ was calculated as $\underline{I} = \underline{I}_p - 2(B.L. + B.R.)$, where $\underline{I}_p$ = the intensity of the peak, B.L. = left background and B.R. = right background. The scan interval was extended by 25 % at both ends for the background measurement. All data sets were corrected for absorption (except for compound VI due to loss of the crystal), Lorentz and polarisation effects. The absorption coefficient for the neutron diffraction study was calculated from measurements on two crystals.

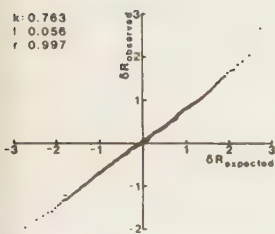
Determination and refinement of the structures

The S-atoms in $\text{LiS}_2\text{CN}(\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$ were located from a three-dimensional vector map and the other atoms from subsequent difference Fourier syntheses. All other structures were determined by direct methods⁶⁰ and difference Fourier calculations.

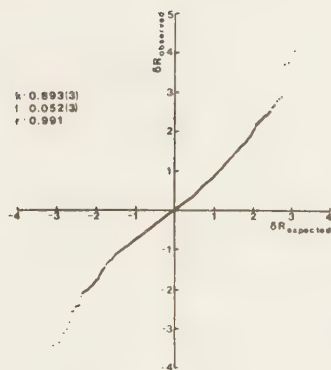
The structures were refined using full-matrix least-squares, minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $w^{-1} = (\sigma_c^2(\underline{I})/4|F_o|^2 + C1|F_o|^2 + C2)$. Data concerning the refinements are given in Table 2. The atomic scattering factors with corrections for anomalous dispersion were taken from International Tables for X-ray Crystallography.⁶¹ The coherent scattering amplitudes for the neutron data refinement were taken from Bacon.⁶² In order to compare model and experiment, δR -plots⁶³ were made for all refinements (Fig. 5). All plots are approximately straight lines through the origin and with slopes close to unity, indicating good fits between the structural models and the experiments.

ESCA

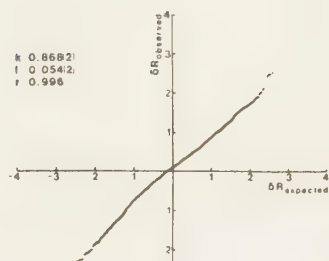
ESCA-measurements on compounds I (273 K), II (103, 273 K), III (273 K) and $\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$ (Kebo-Grave) (273 K) were recorded on an AEI ES 200 Photoelectron Spectrometer. The spectra were evaluated by the method of internal calibration developed by Larsson & Folkesson.⁶⁴⁻⁶⁶ This method uses the C_6H_5 -group as standard. The charges on the atoms in the dithiocarbamate ions are calculated by assuming that the charge on Na^+ is exactly +1. The value of $E_b(\text{Na}1s) = 1071.1 \text{ eV}$ for Na^+ is related to $(\text{C}_6\text{H}_5)_4\text{P}^+$ via F^- in $(\text{C}_6\text{H}_5)_4\text{PF}$ and NaF . The results are given in Table 3.



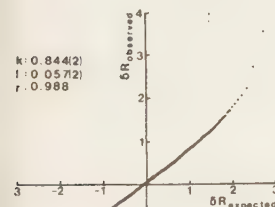
I (Neutrons)



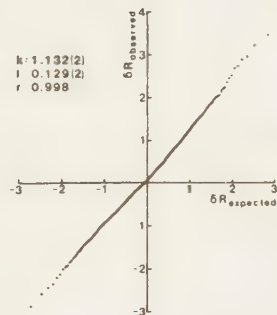
II



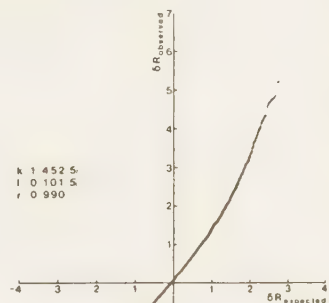
III



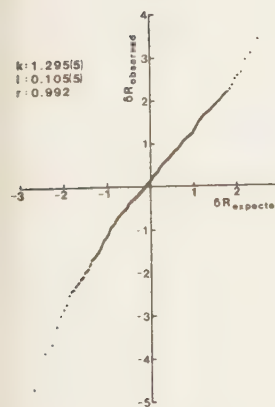
IV



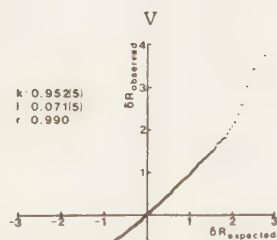
V



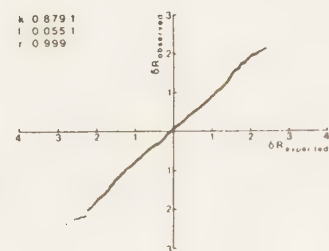
VI



VIII



IX



VII

Fig. 5 δR -plots comparing obs. and calc. structure amplitudes. For denotations see Table 1. $y=kx+l$, r =correlation coefficient.

Table 3. Effective charges on the atoms in the four Na^+ -compounds. The values are based on two separate ESCA-measurements.

	q_S	q_N	q_C
$\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$	-0.46(3) -0.46(3)	-0.24(2) -0.24(2)	0.05(1) 0.05(1)
$\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$	-0.43(3) -0.43(3)	-0.21(2) -0.21(2)	0.07(1) 0.07(1)
$\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$	-0.43(3) -0.43(3)	-0.21(2) -0.21(2)	0.06(1) 0.07(1)
$\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$	-0.31(3) -0.34(3)	-0.27(2) -0.28(2)	0.03(1) 0.03(1)

DESCRIPTION OF THE STRUCTURES

The structures are described in detail in refs. 1-7 and 9-11. In this chapter common characteristics of the packing and linking of the building blocks in the structures will be given together with a short account for the effect of the temperature on the observed structure of $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$.

The structures of $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$ (I) and $\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ (II) are very similar. Four water O-atoms and two S-atoms (from different ligands) surround the sodium ion forming a distorted octahedron. These polyhedra share corners at the S-atoms and edges at O-atoms, forming layers parallel to the ab-plane (Fig. 6).

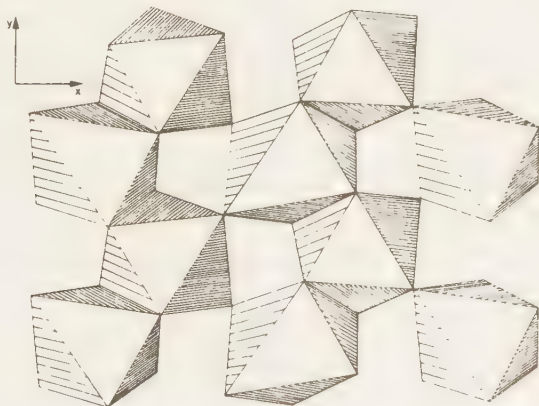


Fig.6

The polyhedron layer in $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$.

Both S-atoms of the dtc ion are hydrogen bonded to the coordination polyhedra. The hydrophobic parts of the dtc ligands are directed along c and the structure may be described as van der Waals packed triple layers, composed of "dtc ions-coordination polyhedra-dtc ions" (Fig. 7).

In $\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$ (III) sodium coordinates six water O-atoms forming a distorted octahedron. The coordination polyhedra form pairs by edge-sharing and these pairs are connected to layers parallel to the ab-plane by hydrogen bonds (Fig. 8).

Both S-atoms in the dtc ion are hydrogen bonded to the coordination polyhedra layer with its hydrophobic parts directed along c. The structure is thus composed of van der Waals packed triple layers, similar to those in I and II (Fig. 7).

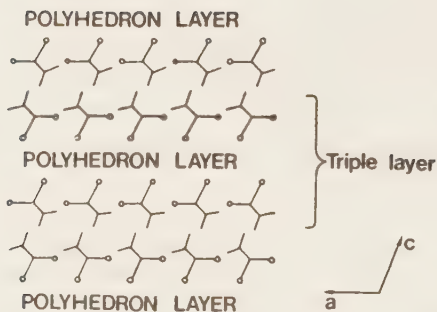


Fig.7 The triple layer.

The Li-dtc hydrates contain no Li-S bonds and the dtc ions are connected to the coordination polyhedra solely by hydrogen bonds. In $\text{LiS}_2\text{CN}(\text{CH}_2)_4 \cdot 4\text{H}_2\text{O}$ (IV) and $\text{LiS}_2\text{CN}(\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$ (V) lithium coordinates four water O-atoms as a distorted tetrahedron. The tetrahedra are connected to a three-dimensional network by hydrogen bonds. The hydrofobic parts of the dtc ions form van der Waals packed stacks in channels running along b (IV) or c (V) (Figs. 9-10).

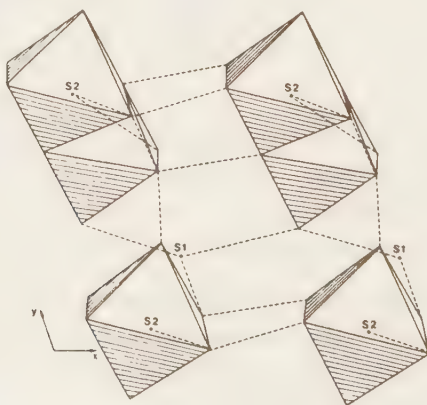


Fig.8 The polyhedron layer in $\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$. Dotted lines indicate hydrogen bonds.

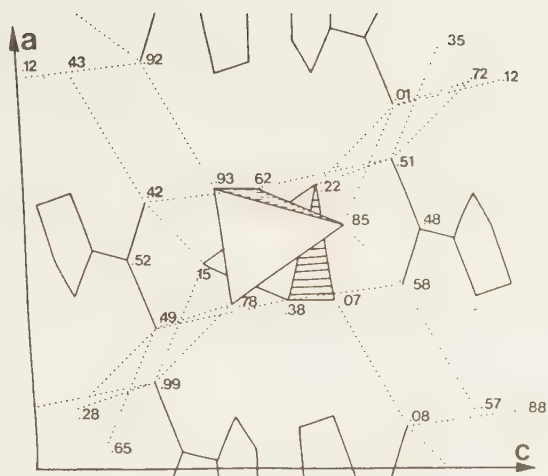


Fig.9 The structure of $\text{LiS}_2\text{CN}(\text{CH}_2)_4 \cdot 4\text{H}_2\text{O}$. Dotted lines indicate hydrogen bonds.

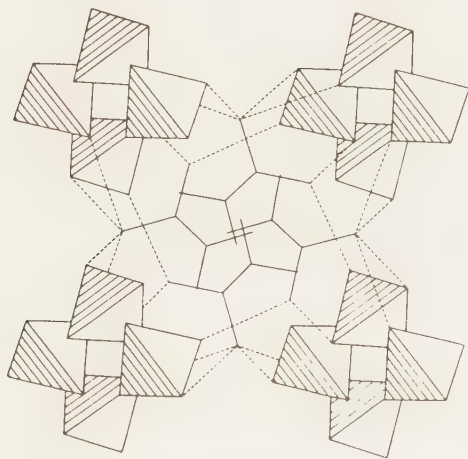


Fig.10 The structure of $\text{LiS}_2\text{CN}(\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$ viewed along the c -axis. Dotted lines indicate hydrogen bonds.

In $\text{LiS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$ (VI) and $\text{LiS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 3\text{H}_2\text{O}$ (VII) pairs of $[\text{Li}(\text{H}_2\text{O})_4]^+$ -tetrahedra are formed by edgesharing. In the former compound the pairs are connected to chains along a by hydrogen bonds between adjacent pairs. As in IV and V the chains are cross-linked by hydrogen bonds to a three-dimensional network, containing channels of van der Waals packed dtc ions.

The pairs of Li-tetrahedra in VII are connected to layers parallel to the ab-plane by hydrogen bonds. The hydrophobic parts of the dtc ions are directed along c and the structure may be described as consisting of van der Waals packed triple layers similar to those in the Na-dtcs.

The crystal structure of I has been investigated at 295, 150 and 27 K with X-rays and at 295 K with neutrons. The most significant change observed with decreasing temperature is a contraction of the coordination polyhedron. The sum of the six Na-X distances is 0.168 Å smaller at 27 K than at 295 K. It should also be noted that the coordination polyhedron becomes more symmetric at 27 K than at 295 K (i.e. the distances and angles are more uniform at the lower temperature). The four S...O distances in the S...H-O hydrogen bonds are influenced in the same way, $\Sigma \text{S...O}$ is 0.121 Å smaller at 27 K than at 295 K. In the $\text{S}_2\text{CN}(\text{CH}_2)_4$ -group there is a slight trend towards longer distances at low temperatures, but the only significant elongation occurs for the C(4)-C(5) distance (Fig. 11), which is 0.12 Å longer at 27 K as compared to 295 K. The short bond distance observed at 295 K and 150 K is caused by a conformational re-orientation of the pyrrolidine-ring. At 27 K one conformer is clearly resolved and the observed C-C distance is thus "normal". A simplified picture of the conformational reorientation is shown in Fig. 11.

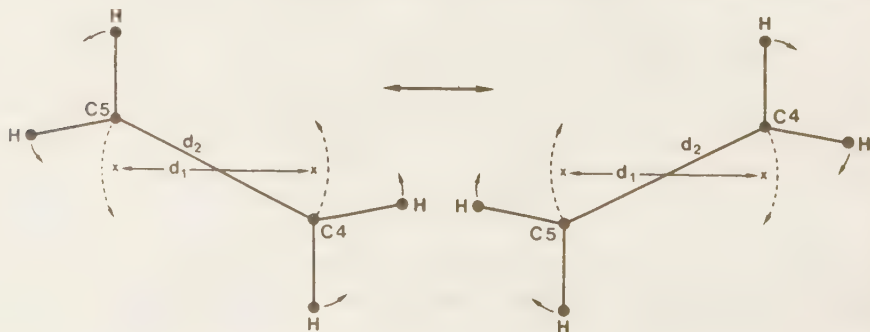


Fig.11

The dotted line indicates the path for actual atomic movements and the crossed mark expected experimentally observed atomic positions. The distance d_1 is shorter than d_2 as observed.

The two different types of structures in the alkali dtc hydrates are clearly reflected in the shapes of the macroscopic crystals. Those involving layered structures are very thin along the axis perpendicular to the layer plane, while the others have a more three-dimensional habitus.

The crystal structure of $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_2)_3$ is similar to that observed in other $\text{Fe}(\text{III})$ dtcs.¹² Iron coordinates three dtc ligands as chelates, forming an octahedron, somewhat distorted towards a trigonal prism (Fig. 12). These polyhedra, with their hydrofobic parts directed away from iron, are van der Waals packed throughout the structure.

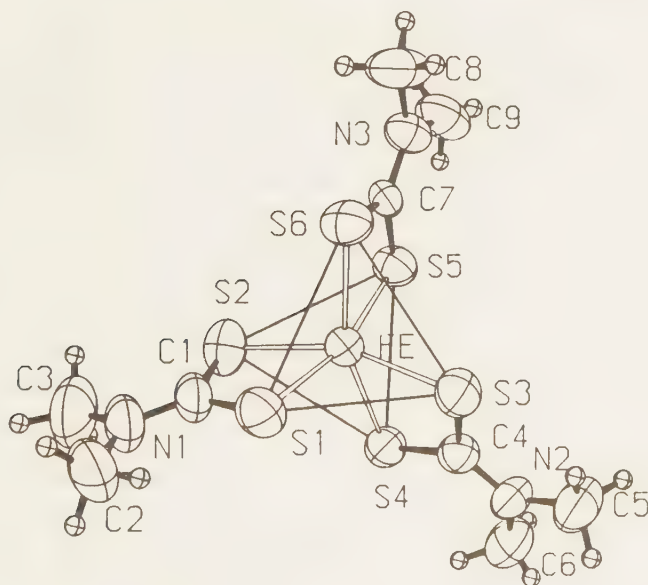
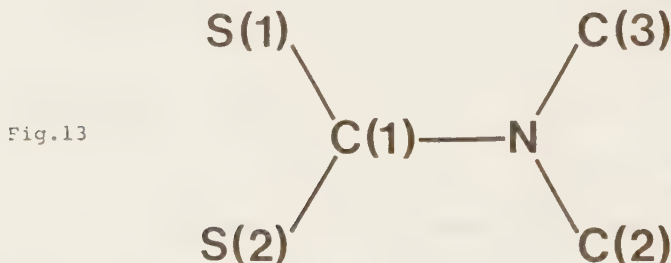


Fig.12 The coordination polyhedron in $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_2)_3$ at 400K.

THE GEOMETRY OF THE S_2CNC_2 -MOIETY

The discussion will be based on the structural parameters for Li^{5,9-11} Na^{1,3-4,7,71} and some NH_2R_2 -dtc compounds⁶⁷⁻⁷⁰ (Table 4) unless otherwise stated. The numbering of the atoms in the S_2CNC_2 -moiety is given in Fig. 13.



Bond distances

Due to the different environments for the two S-atoms in a dtc ion, the difference between the two S-C(1) distances may be as large as 0.01 - 0.03 Å, corresponding to 5 - 30 e.s.d.'s. However, the average S-C(1) distances (i.e. $(S(1) - C(1) + S(2) - C(1))/2$), are not significantly different for the Li and Na dtcs and for the NH_2R_2 -dtcs they are only slightly shorter. The weighted average for all the S-C(1) distances in Table 4a is 1.722(2) Å. A bond order-bond length curve (Fig. 14) has been derived from the data collected in Table 5 and Pauling's equation⁷² $(r_x = r_1 - (r_1 - r_2) \cdot \frac{3x}{2x+1})$, where x is the fractional double bond character (modified to bond orders in Fig. 14) in a bond of length r_x , r_1 is the single bond length and r_2 is the double bond length.

The C(1)-N bond lengths for the 12 ionic dtcs (Table 4a) are not significantly different but they do show a clear trend. For all three cations the value for $\bar{S}_2CN(CH(CH_3)_2)_2$ is the largest and the value for $\bar{S}_2CN(CH_2)_4$ the shortest, with $\bar{S}_2CN(CH_3)_2$ and $\bar{S}_2CN(C_2H_5)_2$ in between. The mean value of 1.333(3) Å for the dtcs is equal to the mean value for three thiuram disulfides⁶ indicating that the drastic rearrangement of the bond orders in the S-C(1) bonds between tdss and dtcs has no detectable effect on the bond order in the C(1)-N bond. A similar bond order-bond length curve as for the S-C bonds has been made for the C-N bonds (Fig. 15) using the bond lengths in Table 5.

Table 4. Structural parameters with e.s.d.'s for the alkaldithiocarbamates. All mean values have been calculated as $\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$ with $\sigma(\bar{x}) = 1 / \sqrt{\sum_{i=1}^n 1/\sigma_i^2}$. Distances are given in Å and angles in degrees.

a) Distances

Compound	S(1)-C(1)	S(2)-C(1)	S-C(1) (Mean)	C(1)-N	N-C(2)	N-C(3)	S(1)...S(2) (Mean)	C(2)...C(3)	S...N (Mean)
NaS ₂ CN(CH ₂) ₄ ·2H ₂ O	1.734(2)	1.711(2)	1.723(1)	1.326(3)	1.478(3)	1.471(4)	3.018(1)	2.427(5)	2.633(2)
LiS ₂ CN(CH ₂) ₄ ·2H ₂ O	1.735(1)	1.720(1)	1.727(1)	1.322(2)	1.474(2)	1.471(2)	2.995(1)	2.425(2)	2.647(1)
[NH ₂ (CH ₂) ₄][S ₂ CN(CH ₂) ₄]	1.732(2)	1.706(3)	1.724(2)	1.326(3)	1.476(4)	1.472(4)	3.003(1)	2.424(5)	2.632(2)
Mean	1.734(1)	1.717(1)	1.726(1)	1.324(1)	1.475(2)	1.471(2)	3.005(1)	2.425(2)	2.642(1)
NaS ₂ CN(C ₂ H ₅) ₂ ·3H ₂ O	1.729(6)	1.712(7)	1.722(5)	1.344(8)	1.479(8)	1.475(9)	2.986(3)	2.482(11)	2.658(4)
LiS ₂ CN(C ₂ H ₅) ₂ ·3H ₂ O	1.724(1)	1.722(1)	1.723(1)	1.337(2)	1.466(2)	1.472(2)	2.967(1)	2.464(2)	2.664(1)
[NH ₂ (C ₂ H ₅) ₂][S ₂ CN(C ₂ H ₅) ₂]	1.731(2)	1.699(2)	1.715(1)	1.349(3)	1.462(3)	1.465(3)	2.978(1)	2.471(5)	2.655(2)
Mean	1.725(1)	1.717(1)	1.721(1)	1.341(2)	1.465(2)	1.470(2)	2.973(1)	2.465(2)	2.662(1)
NaS ₂ CN(CH ₃) ₂ ·2H ₂ O	1.736(2)	1.709(2)	1.722(1)	1.335(3)	1.465(4)	1.460(4)	2.992(1)	2.455(6)	2.650(2)
LiS ₂ CN(CH ₃) ₂ ·4H ₂ O	1.728(2)	1.719(2)	1.723(1)	1.328(3)	1.461(4)	1.460(4)	2.966(1)	2.469(5)	2.658(1)
[NH ₂ (CH ₃) ₂][S ₂ CN(CH ₃) ₂]	1.715(2)	1.706(2)	1.710(1)	1.340(3)	1.459(4)	1.458(4)	2.959(1)	2.456(5)	2.651(2)
Mean	1.726(1)	1.711(1)	1.718(1)	1.335(2)	1.462(2)	1.459(2)	2.972(1)	2.461(3)	2.656(1)
NaS ₂ CN(CH(CH ₃) ₂) ₂ ·5H ₂ O	1.745(6)	1.703(6)	1.724(4)	1.347(7)	1.486(8)	1.485(8)	2.961(3)	2.489(9)	2.678(4)
LiS ₂ CN(CH(CH ₃) ₂) ₂ ·3H ₂ O	1.740(6)	1.709(6)	1.724(4)	1.341(8)	1.508(8)	1.486(9)	2.948(2)	2.518(10)	2.677(4)
[NH ₂ (CH(CH ₃) ₂) ₂][S ₂ CN(CH(CH ₃) ₂) ₂]	1.734(3)	1.701(3)	1.718(2)	1.349(4)	1.486(4)	1.491(4)	2.940(1)	2.494(5)	2.676(3)
Mean	1.737(2)	1.703(2)	1.720(2)	1.347(3)	1.490(3)	1.489(3)	2.943(1)	2.497(4)	2.677(2)

Table 4. continued

b) Angles

Compound	S(1)-C(1)-S(2)	S-C(1)-N (Mean)	C(1)-N-C (Mean)	C(2)-N-C(3)	S(1)-N-S(2)
$\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$	122.3(1)	118.8(1)	124.6(1)	110.8(2)	70.0(1)
$\text{LiS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$	120.2(1)	119.9(1)	124.5(1)	110.8(1)	68.9(1)
$[\text{NH}_2(\text{CH}_2)_4][\text{S}_2\text{CN}(\text{CH}_2)_4]$	121.7(1)	119.1(1)	124.9(2)	110.6(2)	69.6(1)
Mean	121.4(1)	119.6(1)	124.6(1)	110.7(1)	69.5(1)
$\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$	120.4(4)	119.8(4)	122.9(4)	114.3(5)	68.3(1)
$\text{LiS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$	118.8(1)	120.5(1)	123.0(1)	114.0(1)	67.7(1)
$[\text{NH}_2(\text{C}_2\text{H}_5)_2][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$	120.6(1)	119.7(1)	122.4(1)	115.2(2)	68.2(1)
Mean	119.7(1)	120.4(1)	122.8(1)	114.2(1)	68.0(1)
$\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$	120.9(1)	119.5(1)	122.8(1)	114.2(3)	68.9(1)
$\text{LiS}_2\text{CN}(\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$	118.8(1)	120.6(1)	122.2(1)	115.4(2)	67.8(1)
$[\text{NH}_2(\text{CH}_3)_2][\text{S}_2\text{CN}(\text{CH}_3)_2]$	119.7(1)	120.2(1)	122.7(1)	114.7(3)	67.9(1)
Mean	119.8(1)	120.1(1)	122.6(1)	115.0(1)	68.2(1)
$\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$	118.3(3)	120.8(3)	123.1(4)	113.8(5)	67.1(1)
$\text{LiS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 3\text{H}_2\text{O}$	117.5(3)	121.3(3)	122.8(4)	114.5(5)	66.8(1)
$[\text{NH}_2(\text{CH}(\text{CH}_3)_2)_2][\text{S}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2]$	117.7(2)	121.1(1)	123.1(1)	113.8(2)	66.6(1)
Mean	117.8(1)	121.1(1)	123.1(1)	113.9(2)	66.8(1)

Table 4. continued

c) The shortest van der Waals contacts. Since the steric interference between the atoms in the 5-membered ring in $S_2CN(CH_2)_4$ is of no interest, the C...H and H...H values have been omitted. No values for $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ can be given since the coordinates have not been published.

	INTRAMOLECULAR				INTERMOLECULAR	
	S(1)...H	S(2)...H	C...H	H...H	C...H	H...H
$NaS_2CN(CH_2)_4 \cdot 2H_2O$	2.76(4)	2.78(4)	-	-	-	-
"	2.85(1)*	2.84(2)*	-	-	-	-
$LiS_2CN(CH_2)_4 \cdot 4H_2O$	2.75(2)	2.91(2)	-	-	-	-
$[NH_2(CH_2)_4][S_2CN(CH_2)_4]$	2.85**	2.89**	-	-	-	-
$LiS_2CN(C_2H_5)_2 \cdot 3H_2O$	2.58(2)	2.63(2)	2.41(2)	2.24(3)	2.87(2)	2.44(5)
$[NH_2(C_2H_5)_2][S_2CN(C_2H_5)_2]$	2.49**	2.72**	-	-	-	-
$NaS_2CN(CH_3)_2 \cdot 2H_2O$	2.56(5)	2.71(3)	2.45(4)	2.29(7)	3.05(5)	2.66(11)
$LiS_2CN(CH_3)_2 \cdot 4H_2O$	2.76(5)	2.70(4)	2.47(5)	2.18(8)	2.63(6)	2.64(8)
$[NH_2(CH_3)_2][S_2CN(CH_3)_2]$	2.49**	2.54**	-	-	-	-
$NaS_2CN(CH(CH_3)_2)_2 \cdot 5H_2O$	2.48(6)	2.74(9)	2.36(9)	2.04(12)	2.45(12)	3.12(9)
$LiS_2CN(CH(CH_3)_2)_2 \cdot 3H_2O$	2.42(7)	2.85(7)	2.33(6)	2.17(11)	2.42(16)	3.23(7)
$[NH_2(CH(CH_3)_2)_2][S_2CN(CH_3)_2)_2]$	2.38**	2.72**	-	-	-	-

* values from neutron data

** calculated from published data

Table 4. continued

d) Torsion angles and deviations ($\text{\AA} \times 10^4$) from the LS-plane defined by S(1), S(2), C(1) and N. Torsion angles are defined as $\phi_1 = \text{S}(1)\text{-C}(1)\text{-N-C}(2)$, $\phi_2 = \text{S}(2)\text{-C}(1)\text{-N-C}(3)$, $\phi_3 = \text{S}(1)\text{-C}(1)\text{-N-C}(3)$ and $\phi_4 = \text{S}(2)\text{-C}(1)\text{-N-C}(2)$.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	S(1)	S(2)	C(1)	N	C(2)	C(3)
I	-1.2(3)	-2.2(3)	177.3(2)	179.4(2)	0(6)	1(7)	-36(23)	14(21)	571(34)	-141(34)
IV	3.7(2)	2.9(2)	-175.2(1)	-178.2(1)	-3(3)	-4(4)	131(12)	-42(11)	-976(17)	425(15)
VI	2.4(2)	2.6(2)	-174.7(1)	179.6(1)	-5(4)	-6(4)	193(13)	-56(12)	-1053(17)	12(17)
II	-7.0(2)	-12.5(2)	168.6(3)	171.9(3)	2(7)	2(6)	73(22)	-27(21)	-2657(42)	1512(40)
V	-2.7(4)	2.0(4)	180.0(2)	179.3(3)	2(6)	4(8)	-139(26)	43(23)	-57(41)	-226(46)
III	-0.3(8)	0.0(9)	-179.5(5)	179.2(5)	-1(19)	-1(20)	34(62)	-9(50)	-90(71)	-157(72)
VII	4.3(8)	7.4(9)	-174.0(5)	174.3(5)	2(17)	2(17)	-93(60)	261(51)	-1346(71)	1199(73)

Table 5. Some C-S and C-N bond distances (Å) with e.s.d.'s taken from literature.

M.W. = microwave spectrum, E.D. = electron diffraction, X-ray = X-ray diffraction. The mean value 1.475 for the C-N bonds of bond order 1.0 has been calculated from Appendix A.

Compound	Method	Distance	Ref.	Compound	Method	Distance	Ref.
(S-C bond order 2.0)				$\text{Re}(\text{C}_{39}\text{H}_{31}\text{O}_2\text{P}_2\text{S}_2)$	X-ray	1.68(1)	86
CClFS	M.W.	1.595()	73	$\text{Ru}(\text{C}_{38}\text{H}_{32}\text{P}_2\text{S}_4)$	"	1.70(1)	86
CH_3NCS	E.D.	1.597(5)	74	"	"	1.68(1)	86
CH_2SO	M.W.	1.610(2)	75	"	"	1.68(1)	86
Mean		1.600		"	"	1.67(1)	86
(S-C bond order 1.0)				$\text{Ru}(\text{C}_{38}\text{H}_{32}\text{P}_2\text{S}_4)$	"	1.66(2)	87
$\text{C}_6\text{H}_{12}\text{S}_3$	X-ray	1.810(1)	76	"	"	1.66(2)	87
"	"	1.824(1)	76	"	"	1.68(2)	87
"	"	1.812(1)	76	"	"	1.64(1)	87
"	"	1.821(1)	76	$\text{Pt}_2(\text{CH}_3\text{CS}_2)_4$	"	1.672(14)	88
"	"	1.817(1)	76	"	"	1.695(15)	88
"	"	1.821(1)	76	"	"	1.694(14)	88
$\text{C}_3\text{H}_8\text{S}$	M.W.	1.819()	77	"	"	1.684(12)	88
$\text{C}_8\text{H}_{12}\text{S}_6$	X-ray	1.851(4)	78	"	"	1.651(12)	88
"	"	1.816(4)	78	"	"	1.676(13)	88
"	"	1.815(4)	78	"	"	1.678(13)	88
"	"	1.815(4)	78	Mean		1.675	
"	"	1.819(4)	78	(C-N bond order 2.0)			
"	"	1.835(4)	78	$\text{C}_6\text{Cl}_2\text{F}_5\text{N}$	E.D.	1.224(10)	89
$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_4$	"	1.820(6)	79	CH_3N	M.W.	1.257()	90
"	"	1.831(6)	79	$\text{C}_7\text{H}_{12}\text{N}_2\text{S}_2$	X-ray	1.272(3)	91
$\text{C}_3\text{H}_9\text{BS}_2$	E.D.	1.818(6)	80	$\text{C}_{10}\text{H}_{20}\text{N}_2$	E.D.	1.283(6)	92
$\text{C}_2\text{H}_6\text{S}_2$	"	1.816(3)	81	Mean		1.259	
$\text{C}_3\text{H}_8\text{S}_2$	"	1.817(4)	81	(C-N bond order 1.5)			
$\text{C}_4\text{H}_8\text{S}_2$	"	1.817(5)	82	$\text{C}_5\text{H}_5\text{N}$	X-ray	1.34	93
"	"	1.812(5)	82	$\text{Ag}(\text{C}_5\text{H}_5\text{N})_4 \cdot \text{ClO}_4$	"	1.324(6)	94
$\text{C}_2\text{H}_6\text{S}$	"	1.805(2)	83	"	"	1.339(5)	94
$\text{C}_5\text{H}_7\text{HgSO}$	"	1.804(3)	84	$\text{Cu}(\text{C}_5\text{H}_5\text{N})_4 \cdot \text{ClO}_4$	"	1.339(8)	94
Mean		1.818		"	"	1.342(7)	94
(S-C bond order 1.5)				Mean		1.337	
$\text{Re}(\text{C}_{39}\text{H}_{31}\text{O}_2\text{P}_2\text{S}_2)$	X-ray	1.64(2)	85				

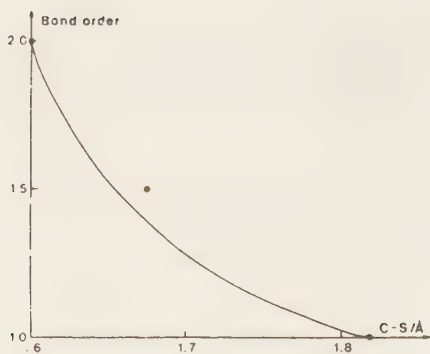


Fig.14

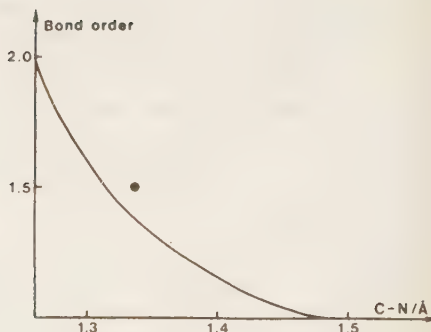


Fig.15

Bond order - bond length curves for C-S and C-N bonds.

In Table 6 bond orders for the C(1) bonds in a number of dithio compounds are estimated from Figs. 14-15. The sum of the bond orders should be 4.0 whereas Pauling's equation seems to give a slight underestimate. This is further accentuated by the fact that the mean values for the bond distances corresponding to bond order 1.5 in Table 5 are larger than the values found in Figs. 14-15.

The N-C(2) and N-C(3) distances are of the magnitude expected.¹⁰¹ They increase as the number of carbon atoms bonded to C(2) and C(3) increase i.e. as $R_2 = (\text{CH}_3)_2 < (\text{C}_2\text{H}_5)_2 \sim (\text{CH}_2)_4 < (\text{CH}(\text{CH}_3)_2)_2$.

Planarity

It has been proposed¹⁰² that the planarity of the S_2CNC_2^- moiety in the dtcs should be of importance in determining the magnetic properties of Fe(III)-dtcs. If so the torsion angles S-C(1)-N-C and the deviations from the LS-plane defined by S(1), S(2), C(1) and N (or S(1), S(2), C(1), N, C(2) and C(3)) should be strongly correlated to τ_{eff} of the Fe(III) complex. No such correlations have been observed for the dtc ligands discussed here. The deviations from planarity are small for all 12 dtc ions as shown by the sum of angles around C(1) and N, which are close to 360° (Table 4b). The small deviations

Table 6. Bond orders for some dithio compounds. The values have been estimated from the funtions in Figs. 14-15. For the calculation of the C-O and C-C bond orders with Paulings equation the values of C = O = 1.185, C - O = 1.437, C = C = 1.34, C - C = 1.48 have been taken from reference 72 and 93.

	C-S/Å	Bond order	C-X/Å	Bond order	Bond order sum	Ref.
$[(C_2H_5)_4N]_2[Ni(S_2CC_5H_4)_2]$	1.737	1.17	1.381	1.39	3.73	95
$Fe(S_2CN(CH_2)_4)_3$	1.712	1.25	1.317	1.48	3.98	96-98
Alkali-DTC	1.722	1.21	1.333	1.40	3.82	Table 4
TDS (S=C)	1.647	1.52	1.333	1.40	3.92	6
TDS (S-C)	1.807	1.00	1.333			
$Fe(S_2CSC_4H_9)_3$	1.693	1.30	1.713	1.24	3.84	72
$Fe(S_2COC_2H_5)_3$	1.684	1.35	1.328	1.23	3.93	99
$M(S_2CCH_3)_n$	1.676	1.37	1.509	1.00	3.74	88
$Fe(S_2CN(CH)_4)_3$	1.686	1.35	1.365	1.26	3.96	100

are not restricted to a certain ion, but vary rather randomly within the series (Table 4d).

Non-bonded distances, angles and steric interference

Significant variations between the investigated dtc ions are observed in the non-bonded distances $S(1)...S(2)$, $S(1)...N$, $S(2)...N$ and $C(2)...C(3)$ and in the angles $S(1)-C(1)-S(2)$, $S(1)-C(1)-N$, $S(2)-C(1)-N$, $S(1)-N-S(2)$ and $C(2)-N-C(3)$ (Table 4a-b). The $S(1)...S(2)$ distance decrease and the $S...N$ and $C(2)...C(3)$ distances increase in the series $R_2 = (CH_2)_4$, $(CH_3)_2$, $(C_2H_5)_2$, $(CH(CH_3)_2)_2$. The variation in the $N-C(2)$ and $N-C(3)$ distances is not sufficient to explain the increase in the $C(2)...C(3)$ distance. In $^-S_2CN(CH_2)_4$ the strained 5-membered ring restricts the $C(2)...C(3)$ distance to about 2.425 Å, but in the other three dtc ions there are no such restrictions. In spite of this the values observed for $^-S_2CN(CH(CH_3)_2)_2$ are significantly larger than those observed for $^-S_2CN(CH_3)_2$ and $^-S_2CN(C_2H_5)_2$ (Table 4a). It is reasonable to assume that these variations are caused by steric interactions. In Table 4c the shortest $C...H$, $S...H$ and $H...H$ distances are given. In all compounds the intramolecular distances are shorter than the intermolecular distances, indicating that the intramolecular interaction is stronger than the intermolecular. Furthermore the dtc ion with the smallest $S(1)...S(2)$ distance, $^-S_2CN(CH(CH_3)_2)_2$, also has the shortest $S...H$ distances and the one with the largest $S(1)...S(2)$ distance has the largest $S...H$ distances. Thus it seems very likely that an intramolecular steric interference $C-H...S$ is responsible for the observed variation in the $S(1)...S(2)$ distance in the series $R_2 = (CH_2)_4$, $(CH_3)_2$, $(C_2H_5)_2$, $(CH(CH_3)_2)_2$.

A convincing way to study the variation in steric interference for different substituents is with space filling precision models. A simplified picture of the steric interference is given in Fig. 16. As the substituents become bulkier in the series $R_2 = (CH_2)_4 < (CH_3)_2 \sim (C_2H_5)_2 < (CH(CH_3)_2)_2$, the atoms $C(2)$ and $C(3)$ move apart increasing the $S...H$ interactions which results in a decrease of the $S(1)-C(1)-S(2)$ angle (Table 4b). Since the steric interaction produces a variabel number of $S...H$ interactions it is not easily described by a single parameter. However, there is a highly significant correlation between the average $S(1)...S(2)$ and $C(2)...C(3)$ distances for the dtcs listed in Table 4a (Fig. 17) supporting the model of intramolecular steric interference.

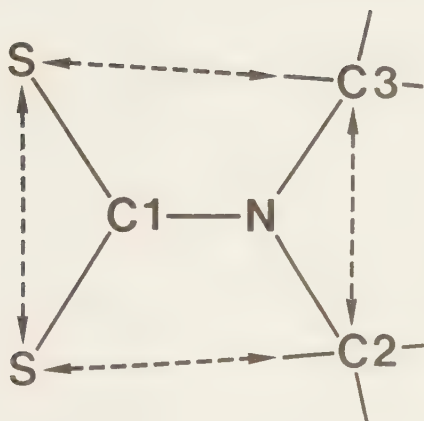


Fig.16 A simplified picture of the intramolecular steric interference.

Another factor reflecting the steric interaction is the correlation between the angles $S(1)-C(1)-S(2)$ and $C(2)-N-C(3)$ within each of the four dtc ions. The structural parameters for all relevant dtc compounds, with $R_2 = (CH_2)_4$, $(CH_3)_2$, $(C_2H_5)_2$ and $(CH(CH_3)_2)_2$, investigated up to 1982, have been collected from the Cambridge Crystallographic⁵⁵ and Chemical Abstracts data bases. Bond distances and bond angles for 86 compounds are given in Appendix A. For each of the four dtc ions the linear correlations between all these parameters have been tested by linear regression. The largest correlation coefficients r and r_w were for all four ligands observed for the function $S-C-S = f(C-N-C)$ (Fig. 18). r and r_w increase as $R_2 = (CH_2)_4 < (CH_3)_2 < (C_2H_5)_2 < (CH(CH_3)_2)_2$, thus supporting the model of $S...H$ interference.

The influence from different metal ions

The compounds given in Appendix A have been divided into three groups according to the type of the coordinating metal ion. Type 1 are weakly coordinating metal ions with ionic character, type 2 are p-block or d-block metals with filled d-orbitals and type 3 are d-metals with partly filled d-orbitals. In compounds with type 1 and 2

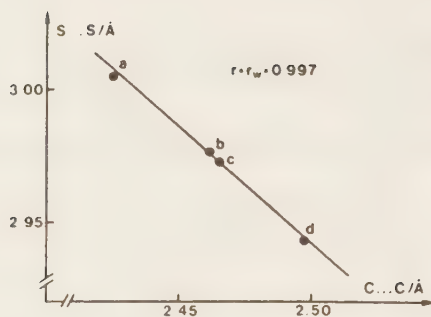
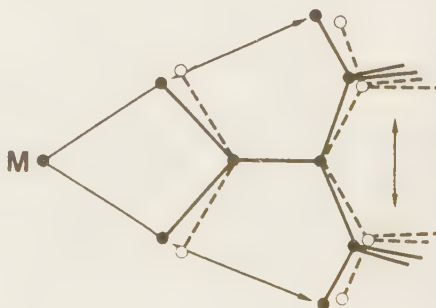


Fig.17 $S(1) \dots S(2) = f(C(2) \dots C(3))$. Points a,b,c and d represent $S_2CN(CH_2)_4$, $S_2CN(CH_3)_2$, $S_2CN(C_2H_5)_2$ and $S_2CN(CH(CH_3)_2)_2$, respectively.

metals the S-C-S angles are all rather large compared to those containing type 3 metals, while the C-N-C angles vary in the reverse order. The variations in the S-C-S angle may be viewed in Fig. 19, where histograms for 408 dtc ions are shown. Shaded areas contain type 3 metals and blank areas contain type 1 and 2 metals. Obviously metal ions containing empty d-orbitals suitable for bonding interact more strongly with the dtc ions than those with completely filled d-orbitals.

It is concluded that the geometry of the S_2CNC_2 -moiety is affected by the coordinating metal ion, as well as the intramolecular steric interference. The combined effect is illustrated in Fig. 20

Fig.20 The combined effect of steric interference and metal coordination. The dotted lines indicates the uncoordinated ligand.



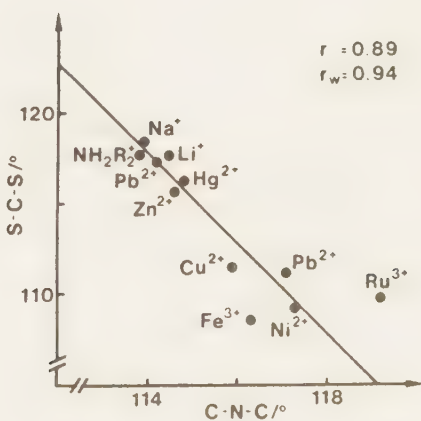
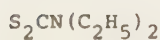
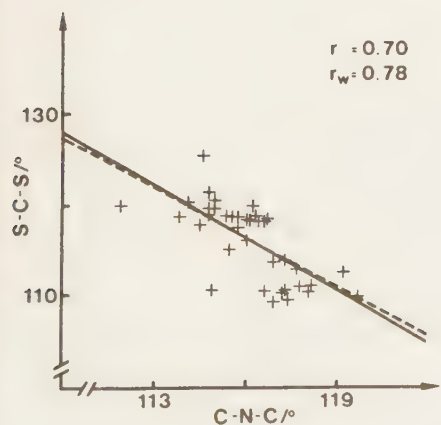
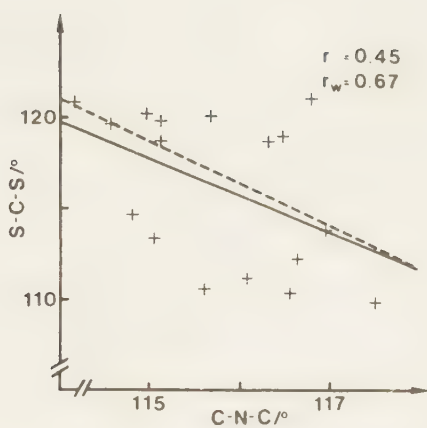
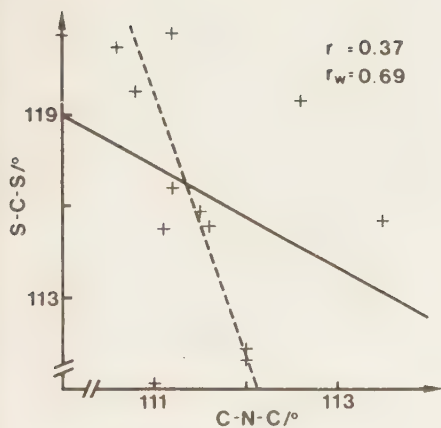


Fig. 18 $S-C-S=f(C-N-C)$. r is the unweighted correlation coefficient and r_w is the weighted correlation coefficient. Dotted lines refer to the weighted analyses.

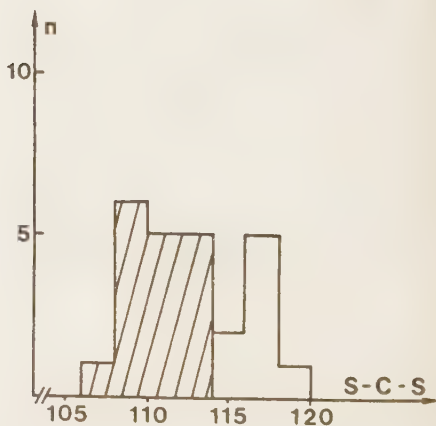
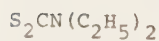
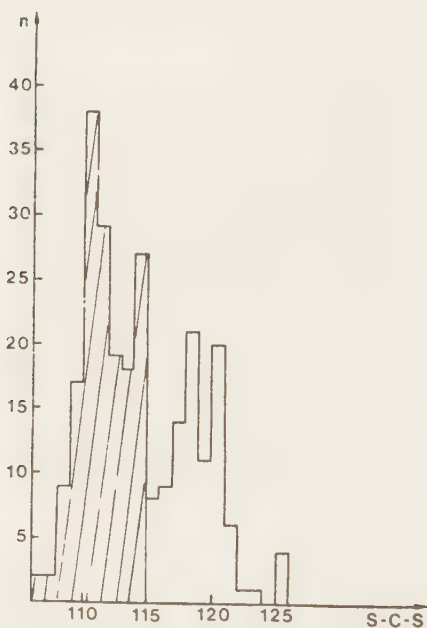
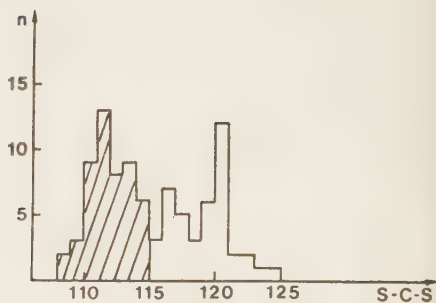
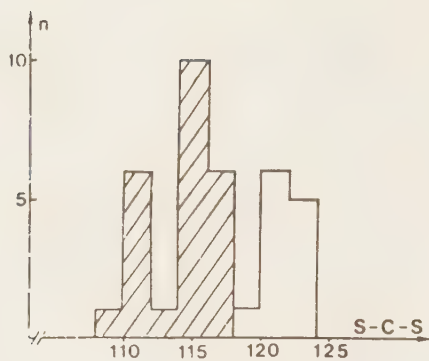


Fig.19 Histograms showing the variations in the S-C-S angle. Shaded areas contain type 3 metals and blank areas contain type 1 and 2 metals (see Appendix A).

ELECTRONIC FEATURES OF THE DITHIOCARBAMATE IONS

The electronic features of the dtc ions are often discussed in terms of the two canonical forms given in Fig. 21. Some authors^{100,102-107} relate the LS behaviour of Fe(III) dtcs to form a) and the HS behaviour to form b), while others are of the opposite opinion.^{41,108}

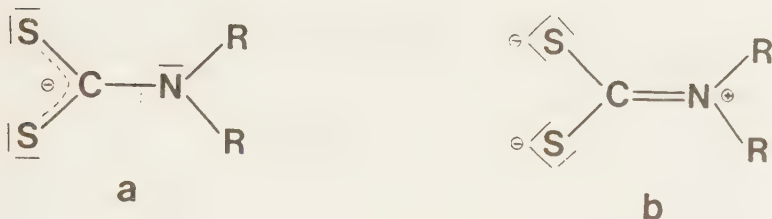


Fig.21

The charges on the atoms derived from ESCA-measurements are given in Table 3. The peaks for the S-atoms are symmetric with half-widths of 2.6 eV for all investigated compounds, indicating equal charges on the two S-atoms in each compound. The difference in charge on the S-atoms between $\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$, -0.31, and the others, -0.43 to -0.46, is highly significant. This difference was further tested by a measurement on a mixed sample of $\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$ and $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$. As expected, the half-widths for the S and N peaks increased (0.15 eV), indicating overlapping peaks. Since $\text{S}_2\text{CN}(\text{CN}(\text{CH}_3)_2)_2$ forms a LS Fe(III)-compound and $\text{S}_2\text{CN}(\text{CH}_2)_4$ forms a HS Fe(III)-compound, it is concluded that a low sulphur charge favours the LS state and a high charge favours the HS state. A comparison between different Fe(III)dithio compounds (Fig. 22) leads to the same conclusion.

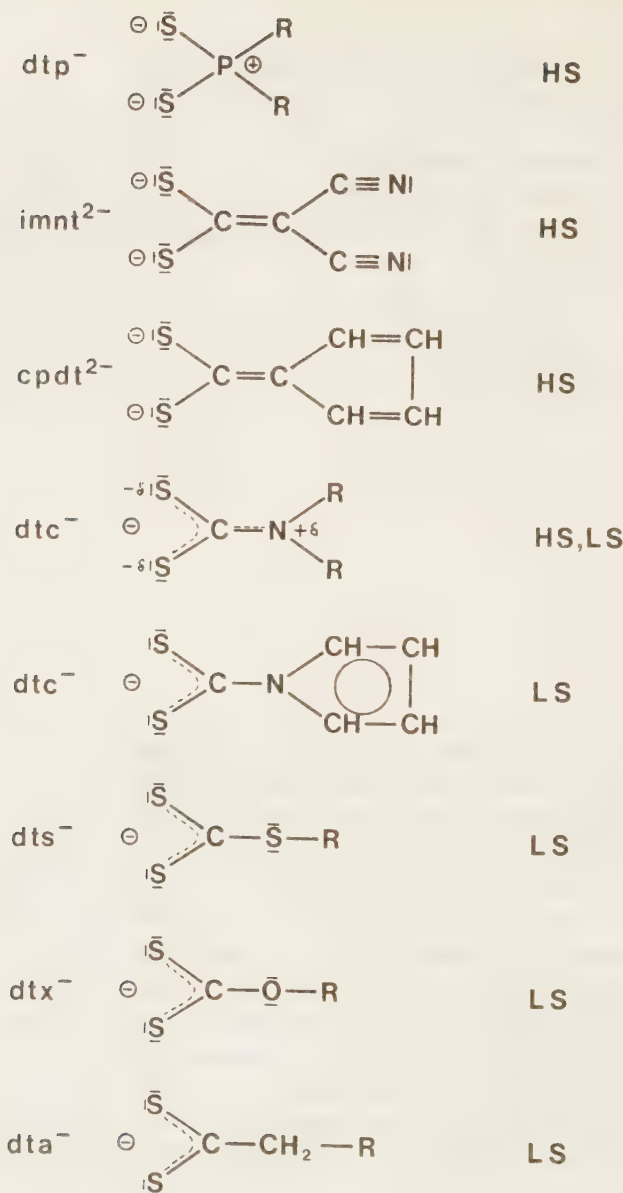


Fig.22 A number of dithio ligands arranged according to the spectrochemical series¹⁰⁹ : dithiophosphate(dtp^-)⁴¹, 1,1-dicyanoethylene-2,2-dithiol(imnt^{2-})¹¹⁰, cyclopentadienedithiocarboxylate(cpdt^{2-})¹⁰⁹ < dithiocarbamate(dtc^-) < xanthate(dtx^-)⁹⁹, thioxanthate(dts^-)⁷² < dithiocarboxylate(dta^-)¹⁰⁶. The magnetic properties of their corresponding Fe(III) compounds are also given. Obviously the smaller the charge on the S-atom, the stronger the ligand field.

A MODEL FOR THE INFLUENCE OF THE SUBSTITUENTS ON THE MAGNETIC PROPERTIES OF TRIS(DITHIOCARBAMATO)IRON(III) COMPOUNDS

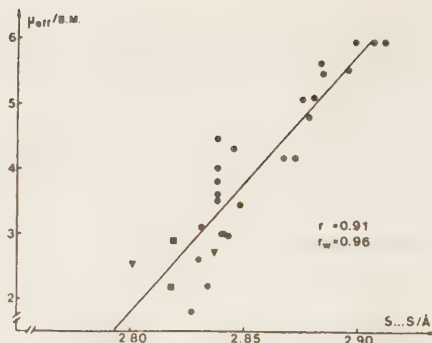
The crystal structure of $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_2)_3$ was studied at 400 ($\mu_{\text{eff}} = 4.83$ B.M.) and 25 K ($\mu_{\text{eff}} = 1.8$ B.M.). Within the FeS_6 -core significant differences between the two temperatures were observed for the Fe-S distances, the S-Fe-S angles and the torsion angles between opposite triangular faces in the coordination polyhedron (Fig. 12) and within the ligand for the angles S-C-S and C-N-C. For 25 accurately determined crystal structures these five parameters are correlated to μ_{eff} with correlation coefficients: $r_{\text{Fe-S}} = 0.94$, $r_{\text{S-Fe-S}} = 0.92$, $r_{\text{torsion}} = 0.72$, $r_{\text{S-C-S}} = 0.87$ and $r_{\text{C-N-C}} = 0.70$.^{8,12} Thus there is a strong correlation between μ_{eff} and those intraligand parameters, which are affected by the intramolecular steric interference. Large steric interferences give small ligand bites and LS, while small steric interferences give large ligand bites and HS compounds. From the ESCA-measurements on the Na-dtcs it was concluded that small ligand bites are associated with smaller charges on the S-atoms than those for large ligand bites. The variation in charge on the S-atoms may be explained by simple electrostatic arguments. A decrease in the S...S distance increases the electrostatic repulsion between the two S-atoms, resulting in a transfer of charge from the S-atoms towards the N-atom, thus favouring canonical form a) in Fig. 21.

Two compounds containing aromatic ring systems, $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_4)_3$ ¹⁰⁰ and $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_5))_3$ ¹¹¹ exhibit LS behaviour, which cannot be explained by steric effects. Actually these compounds do not fit the same function $\mu_{\text{eff}} = f(\text{S-C-S})$ as the other investigated Fe(III)-dtcs. Compared to the others, the S-C(1) distances are shorter and the C(1)-N distances longer, suggesting that aromatic systems disfavour canonical form b) in Fig. 21. The shorter S-C(1) distances may result in a smaller ligand bite and thus comparatively small charges on the S-atoms, without decreasing the S-C(1)-S angle in the same way as for the other studied Fe(III)-dtcs. Fig. 23 shows the correlation between the distance S...S and μ_{eff} for the 25 Fe(III)-dtcs, the two previously described Fe(III)-dtcs with aromatic substituents and the two LS compounds $\text{Fe}(\text{S}_2\text{CS}(\text{C}_4\text{H}_9))_3$ ⁷² and $\text{Fe}(\text{S}_2\text{CO}(\text{C}_2\text{H}_5))_3$.⁹⁹ They all fit the curve rather well and it is concluded that the ligand bite, S...S, is important for μ_{eff} , not only for most Fe(III)-dtcs but also for other tris(dithioato)iron(III) compounds.

Fig.23 $\mu_{\text{eff}} = f(S \dots S)$ for 29

Fe(III) dithio compounds.

Squares represent $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)_4)_3$ and $\text{Fe}(\text{S}_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_5))_3$ and triangles $\text{Fe}(\text{S}_2\text{CS}(\text{C}_4\text{H}_9))_3$ and $\text{Fe}(\text{S}_2\text{CO}(\text{C}_2\text{H}_5))_3$.

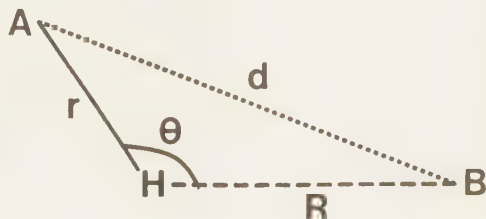


In conclusion, the most important ligand specific factor determining the spin state of iron(III) is the ligand bite, $S \dots S$, which is intimately related to the charges on the S-atoms. Bulky substituents give strong steric interferences and small ligand bites, which produce strong ligand fields and Fe(III) becomes LS. When the steric interference is weak the resulting large ligand bites produce weak ligand fields and Fe(III) becomes HS. Intermediate steric interference will produce intermediate ligand fields and Fe(III) will exhibit CO behaviour. Compounds with aromatic substituents and weak steric interference are LS caused by a withdrawal of electron density from the S-atoms, resulting in small charges on the S-atoms and a small ligand bite, $S \dots S$. This model, including the effect of solvate molecules on the magnetic moment μ_{eff} , is discussed by Ståhl.¹²

HYDROGEN BONDS

All the investigated Na^+ and Li^+ dtcs crystallize as hydrates. The water molecules play an important role as building blocks in the structures through hydrogen bonding (see DESCRIPTION OF THE STRUCTURES). The geometric parameters describing a hydrogen bond are given in Fig. 24. When X-ray methods are used there is a systematic error in the positions of the hydrogen atom resulting in an underestimate of the distance r and consequently the angle θ will be overestimated. A hydrogen bond exists if R is less than the sum of the van der Waals radii of H and B or if d is less than the sum of the van der Waals radii of A and B i.e. for $\text{O}\dots\text{H-O}$: $R < 2.5 \text{ \AA}$ or $d < 3.1 \text{ \AA}$ and for $\text{S}\dots\text{H-O}$: $R < 3.0$ or $d < 3.6 \text{ \AA}$.¹¹²

Fig.24 Geometric parameters describing a hydrogen bond.



The geometry of the $\text{O}\dots\text{H-O}$ bonds are given in Table 7. They show no unusual features and since this type of hydrogen bonds have been frequently studied⁴⁴⁻⁴⁶ they will not be discussed here.

The geometry of the $\text{S}\dots\text{H-O}$ bonds are given in Table 7. The $\text{S}\dots\text{O}$ as well as the $\text{S}\dots\text{H}$ distances are significantly smaller than the sum of the van der Waals radii of the involved atoms. The geometrical criterion for a hydrogen bond is thus fulfilled. The values of d , R and θ are in the ranges usually found,¹¹³⁻¹²³ although distances as large as $d = 3.6 \text{ \AA}$ ($R = 2.9 \text{ \AA}$) and as small as $d = 2.86 \text{ \AA}$ ($R = 1.92 \text{ \AA}$) have been observed.¹²⁴⁻¹²⁵

The R and d distances in the alkali dtcs are about $0.5 \text{ \AA}$ larger for the $\text{S}\dots\text{H-O}$ hydrogen bonds than for the $\text{O}\dots\text{H-O}$ bonds i.e. about the same as the difference in van der Waals radii between S and O.¹¹² The θ angles are of the same magnitude for both types of bonds. These observations indicate that there is no large difference in bond strength between these types of $\text{S}\dots\text{H-O}$ and $\text{O}\dots\text{H-O}$ bonds, which also is supported by spectroscopic evidence.¹²⁶⁻¹²⁸

Table 7. Hydrogen bond distances (Å) and angles (°) with e.s.d.'s.

Compound	S...O	S...H	S...H-O	O...O	O...H	O...H-O
I (295 K)	3.290(2) 3.254(2) 3.208(2) 3.304(2)					
I (Neutrons)	3.291(8) 3.251(8) 3.209(9) 3.308(9)	2.343(11) 2.290(11) 2.222(11) 2.359(12)	170.9(7) 174.9(7) 173.5(7) 167.9(8)			
I (150 K)	3.276(2) 2.239(2) 3.195(3) 3.293(3)					
I (25 K)	3.249(6) 3.204(6) 3.180(9) 3.302(11)					
II	3.210(2) 3.261(2) 3.283(2) 3.312(2)	2.41(4) 2.48(4) 2.47(4) 2.58(4)	173(3) 168(3) 169(4) 164(4)			
$\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$	3.249-3.355					
III	3.305(7) 3.315(7) 3.334(7) 3.352(6) 3.235(7) 3.340(7)	1.94(12) 2.79(16) 2.38(12) 2.78(15) 2.63(14) 2.74(8)	170(8) 174(20) 155(9) 159(17) 150(14) 165(8)	2.821(9) 2.873(8) 2.895(9) 2.780(9)	2.00(12) 2.11(8) 2.21(9) 1.74(11)	164(11) 149(6) 154(9) 170(9)
IV	3.309(2) 3.328(2) 3.369(1) 3.375(2)	2.58(3) 2.54(3) 2.52(3) 2.67(3)	167(3) 163(3) 163(2) 170(3)	2.829(2)	2.02(3)	170(3)

Table 7. continued

Compound	S...O	S...H	S...H-O	O...O	O...H	O...H-O
IV	3.284(1)	2.41(2)	165(2)			
	3.290(2)	2.56(3)	171(2)			
	3.329(2)	2.62(3)	175(3)			
V	3.205(2)	2.56(3)	174(3)	2.823(3)	2.16(4)	160(4)
	3.251(3)	2.40(4)	161(4)	2.912(4)	2.25(5)	156(5)
	3.240(3)	2.36(4)	160(4)			
	3.266(3)	2.46(4)	169(4)			
	3.287(3)	2.62(4)	167(4)			
	3.382(2)	2.50(4)	173(4)			
VI	3.229(1)	2.44(2)	167(2)			
	3.254(1)	2.47(3)	160(3)			
	3.391(2)	2.54(3)	172(3)			
	3.248(2)	2.44(3)	175(3)			
	3.295(2)	2.58(3)	169(3)			
	3.452(2)	2.71(4)	155(3)			
VII	3.203(7)	2.91(12)	107(10)			
	3.274(7)	2.64(11)	141(10)			
	3.303(5)	2.30(9)	152(7)			
	3.214(5)	2.40(7)	168(7)			
	3.224(8)	2.22(11)	170(8)			
	3.362(7)	2.76(8)	150(8)			

THE COORDINATION OF Li^+ AND Na^+

The univalent cations Li^+ ($1s^2$) and Na^+ ($1s^2 2s^2 2p^6$) have closed electron shells and may thus be regarded as positively charged spheres. Coordination numbers reported in the literature range from 4 to 6 for Li^+ and from 4 to 8 for Na^+ .⁵⁰ Table 8 gives bond distances within the coordination polyhedra for the compounds investigated in this study. The coordination numbers are here restricted to 4 for Li^+ and 6 for Na^+ . The observed coordination geometries are best described as (distorted) tetrahedra and octahedra in accordance with simple electrostatic theory (Gillespie and Nyholm).¹²⁹⁻¹³¹ Li^+ only coordinates water molecules and no Li-S bonds are formed. In $\text{LiS}_2\text{CN}(\text{CH}_2)_4 \cdot 4\text{H}_2\text{O}$ and $\text{LiS}_2\text{CN}(\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$ the aqua-complexes are mononuclear while in $\text{LiS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$ and $\text{LiS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 3\text{H}_2\text{O}$ they are binuclear, which is achieved through edgesharing of the coordination polyhedra. For Na^+ the situation is a little more complicated. In $\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$ binuclear aqua-complexes are formed through edgesharing, while in $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaS}_2\text{CN}(\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$ also Na-S bonds are formed. In the latter case each Na^+ coordinates 4 water molecules and 2 sulfur atoms. An infinite layer of coordination polyhedra is formed through edge sharing at water molecules and corner sharing at the two sulfur atoms (Fig. 6). The coordination behaviour observed may be discussed in terms of the hard-soft concept.¹³²⁻¹³³ The Li^+ and Na^+ ions are hard acceptors and the sulfur atom is a soft donor. In the presence of the hard oxygen donor the sulfur atom cannot compete at all for a position in the coordination sphere of Li^+ and sulfur is coordinated to Na^+ only in certain circumstances. An alteration of the packing and hydrogen bond system may prevent sodium-sulfur coordination, as shown by $\text{NaS}_2\text{CN}(\text{CH}(\text{CH}_3)_2)_2 \cdot 5\text{H}_2\text{O}$. The poor affinity of Na^+ and Li^+ to S in dithiocarbamates is also suggested by the work of Uhlin and Åkerström, who encountered large problems when preparing water free Li and Na-dtcs.⁵³ Na-S bonds have also been observed in some other dithiocompounds^{71,134} but are most frequently found in inorganic compounds.^{113,116,117,119,122,125,135-139} The only Li-S bond reported in the literature is for LiHS .¹⁴⁰

As expected the affinity for Li^+ and Na^+ to S in dithiocarbamates is very poor and an eventual metal-ligand bond should have no major effect on the geometry of the dithiocarbamate ligand. Thus the investigated alkali-dtcs are a suitable choice for a study of the geometry of an uncoordinated (free) ligand.

Table 8. Bond distances (Å) with e.s.d.'s in the coordination polyhedra. * X = S.

Compound	Na-X	Compound	
I (295 K)	2.419(2)	NaS ₂ CN(C ₂ H ₅) ₂ ·3H ₂ O	2.360-2.486
	2.365(2)		3.052(3)*
	2.345(2)	III	2.405(7)
	2.502(2)		2.445(6)
	2.997(1)*		2.405(7)
	2.954(1)*		2.432(7)
			2.454(7)
I (N)	2.426(8)		2.392(6)
	2.372(7)		Li-O
	2.349(8)		
	2.500(7)	IV	1.906(3)
	3.007(9)*		1.907(3)
	2.949(9)*		1.923(3)
			2.000(3)
I (150 K)	2.406(3)		
	2.357(3)	V	1.907(5)
	2.342(3)		1.913(5)
	2.480(3)		1.941(5)
	2.982(2)*		1.954(5)
	2.942(2)*		
		VI	1.895(3)
I (27 K)	2.392(6)		1.897(3)
	2.351(7)		2.019(3)
	2.336(5)		2.049(3)
	2.455(8)		
	2.958(6)*	VII	1.870(13)
	2.922(8)*		1.877(13)
			2.011(13)
			2.031(12)
II	2.406(2)		
	2.394(2)		
	2.330(2)		
	2.466(2)		
	2.992(1)*		
	3.015(1)*		

CONCLUSIONS

It has been shown that the S...S distance in the S_2CNC_2 -moiety is very sensitive to the nature of the substituents R and R' in S_2CNRR' . The S...S distance decrease in the series $R_2 = (CH_2)_4$, $(CH_3)_2$, $(C_2H_5)_2$, $(CH(CH_3)_2)_2$, i.e. in the same order as the bulkiness of the substituents increases. This has been interpreted as the results of an increased steric interference, S...H-C, (S...H~2.8 Å for $R_2 = (CH_2)_4$ and S...H~2.4 Å for $R_2 = (CH(CH_3)_2)_2$) in the series above. The S...S distance is intimately associated with the charge on the S-atoms. The smaller the distance the smaller are the charges. These findings have been used to propose a model for the influence of the substituents R and R' on the magnetic behaviour for tris(dithiocarbamato)-iron(III) compounds. Weak steric interference results in large ligand bites and a weak ligand field. The corresponding $Fe(dtc)_3$ compounds will be high-spin. Strong steric interference gives small ligand bites and strong fields. Compounds of this type will be low-spin. Intermediate steric interference produces intermediate fields and the corresponding compounds will exhibit cross-over behaviour. In two low-spin compounds involving aromatic substituents the steric interference is of minor importance. The aromatic substituents in these compounds, however, produce low charges on the S-atoms giving a small S...S distance.

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APPENDIX A

Bond distances (Å) and angles ($^{\circ}$) for the S_2CNC_2 -moiety collected from 86 dithiocarbamate compounds with substituents $R_2 = (CH_3)_4$, $(CH_3)_2$, $(C_2H_5)_2$ or $(CH(CH_3)_2)_2$. Type 1 are weakly coordinating metal ions with ionic character, type 2 are p-block or d-block metals with filled d-orbitals and type 3 are d-metals with partially filled d-orbitals.

P = the number of M-S bonds to each dithiocarbamate ion.

* Not used in the correlation calculations (Fig. 18).

** No coordinates given in the article.

Compound	S(1)-C(1)	S(2)-C(1)	C(1)-N	N-C(2)	N-C(3)	S-C-S	C-N-C	Ref.	P
TYPE 1									
NaS ₂ CN(CH ₂) ₄ · 2H ₂ O, 295 K	1.734(2)	1.711(2)	1.326(3)	1.478(3)	1.471(4)	122.3(1)	110.8(2)	1	2
" 150 K	1.737(3)	1.721(3)	1.318(4)	1.473(4)	1.484(5)	121.8(2)	110.7(3)	1	2
" 27 K	1.745(8)	1.713(7)	1.324(8)	1.490(9)	1.492(9)	122.1(4)	111.3(5)	1	2
" Neutrons	1.732(7)	1.724(9)	1.328(4)	1.464(4)	1.459(6)	122.1(4)	111.9(3)	2	2
KS ₂ CN(CH ₂) ₄ · 1/2H ₂ O (C ₄ H ₁₀ N)(S ₂ CN(CH ₂) ₄)	1.731(9)	1.706(9)	1.327(11)	1.471(13)	1.467(12)	122.1(5)	110.0(7)	3	2
LiS ₂ CN(CH ₂) ₄ · 4H ₂ O	1.732(2)	1.706(3)	1.326(3)	1.476(4)	1.472(4)	121.7(1)	110.6(2)	4	0
"	1.735(1)	1.720(1)	1.322(2)	1.474(2)	1.471(2)	120.2(1)	110.8(1)	5	0
TYPE 2									
Sb(S ₂ CN(CH ₂) ₄) ₃	1.72(1)	1.71(1)	1.34(2)	1.48(2)	1.49(2)	120.0(9)	113.9(1.4)	6	2
"	1.74(1)	1.68(1)	1.32(2)	1.50(2)	1.51(2)	121.2(8)	110.4(1.2)	6	2
"	1.74(1)	1.71(1)	1.33(2)	1.48(2)	1.47(2)	118.6(9)	113.5(1.2)	6	2
Zn(S ₂ CN(CH ₂) ₄) ₂	1.743(7)	1.709(6)	1.322(9)	1.481(8)	1.490(10)	120.0(4)	112.3(6)	7	3
"	1.732(6)	1.717(8)	1.315(10)	1.489(9)	1.487(12)	118.7(5)	110.9(7)	7	2
TYPE 3									
Cr(S ₂ CN(CH ₂) ₄) ₃ · 1/2C ₆ H ₆	1.696(8)	1.711(8)	1.332(8)	1.475(9)	1.481(10)	117.0(5)	111.0(7)	8	2
"	1.704(8)	1.682(8)	1.357(9)	1.467(9)	1.469(10)	115.9(6)	111.4(7)	8	2
"	1.711(8)	1.710(8)	1.335(9)	1.463(10)	1.471(10)	117.9(5)	111.3(8)	8	2
Fe(S ₂ CN(CH ₂) ₄) ₃ · 1/2C ₆ H ₆	1.722(3)	1.703(3)	1.312(4)	1.469(4)	1.472(4)	115.9(2)	110.9(3)	8	2
"	1.705(3)	1.719(3)	1.321(3)	1.476(4)	1.463(4)	116.3(2)	111.3(2)	8	2
"	1.718(3)	1.707(3)	1.319(3)	1.467(3)	1.467(3)	116.0(2)	111.6(2)	8	2
"	1.713(4)	1.708(4)	1.324(6)	1.462(6)	1.478(6)	116.2(3)	111.5(4)	9	2
"	1.715(4)	1.712(4)	1.315(6)	1.475(6)	1.465(6)	115.9(3)	111.9(4)	9	2

$\text{Fe}(\text{S}_2\text{CN}(\text{CH}_2)_3 \cdot 1/2\text{C}_6\text{H}_6$	1.717(4)	1.708(4)	1.321(5)	1.474(5)	1.476(5)	116.2(2)	111.6(3)	9
"	150 K 1.724(6)	1.719(6)	1.317(8)	1.494(8)	1.488(8)	115.6(4)	112.1(5)	9
"	1.716(6)	1.721(6)	1.305(7)	1.471(8)	1.504(8)	115.7(3)	110.8(4)	9
"	1.716(6)	1.733(6)	1.301(7)	1.483(7)	1.488(7)	115.1(3)	110.4(4)	9
$\text{Fe}(\text{S}_2\text{CN}(\text{CH}_2)_4)_3$	1.722(4)	1.725(4)	1.303(5)	1.470(5)	1.481(6)	115.4(2)	110.9(3)	10
"	1.717(4)	1.717(4)	1.323(5)	1.475(6)	1.472(6)	115.6(2)	112.7(3)	10
"	1.720(4)	1.716(4)	1.311(5)	1.477(7)	1.480(6)	115.7(2)	111.2(4)	10
$\text{Cu}(\text{S}_2\text{CN}(\text{CH}_2)_4)_2$	1.713(8)	1.701(7)	1.335(10)	1.52(1)	1.48(2)	115.8(4)	113.5(8)	11
$\text{Ni}(\text{S}_2\text{CN}(\text{CH}_2)_4)_2$	1.707(8)	1.713(8)	1.33(1)	1.50(1)	1.50(1)	111.4(5)	112.0(7)	11
$\text{FeI}(\text{S}_2\text{CN}(\text{CH}_2)_4)_2 \cdot 1/2\text{I}_2$	1.74(1)	1.70(1)	1.30(2)	1.45(2)	1.48(2)	111.5(7)	112(1)	12
"	1.74(1)	1.73(1)	1.28(2)	1.47(2)	1.47(2)	110.4(7)	112(1)	12
$\text{Ir}(\text{S}_2\text{CN}(\text{CH}_2)_4)_3 \cdot 1/2\text{C}_6\text{H}_6$	1.71(2)	1.70(3)	1.31(3)	1.53(4)	1.32(5)	112(2)	115(3)	8
"	1.77(2)	1.72(2)	1.32(3)	1.46(3)	1.44(3)	111(1)	109(2)	8
"	1.80(3)	1.69(3)	1.33(3)	1.39(3)	1.52(3)	109(2)	115(2)	8
$\text{Cu}(\text{S}_2\text{CN}(\text{CH}_2)_4)_2 \cdot \text{ClO}_4$	1.73(1)	1.72(1)	1.28(2)	1.48(1)	1.45(1)	110.1(7)	111(1)	13
"	1.68(1)	1.74(1)	1.32(2)	1.45(1)	1.47(2)	110.4(7)	111(1)	13

R₂ = Dimethyl

Compound	S(1)-C(1)	S(2)-C(1)	C(1)-N	N-C(2)	N-C(3)	S-C-S	C-N-C	ref.	P
TYPE 1									
NaS ₂ CNR ₂ · 2H ₂ O	1.736(2)	1.709(2)	1.335(3)	1.465(4)	1.460(4)	120.9(1)	114.2(3)	14	1
LiS ₂ CNR ₂ · 4H ₂ O	1.728(2)	1.719(2)	1.328(3)	1.460(4)	1.461(4)	118.8(1)	115.4(3)	15	0
[(CH ₃) ₂ NH ₂] ₂ [S ₂ CNR ₂]	1.715(2)	1.706(2)	1.340(3)	1.459(4)	1.458(4)	119.7(1)	114.7(3)	16	0
CsS ₂ CNR ₂	1.716(2)	1.716(2)	1.342(5)	1.456(4)	1.456(4)	121.2(2)	117.5(4)	17	4
TYPE 2									
P(S ₂ CNR ₂) ₃	1.752(8)	1.676(8)	1.32(1)	1.47(1)	1.47(1)	120.5(5)	116.5(7)	18	2
"	1.756(8)	1.676(8)	1.33(1)	1.47(1)	1.46(1)	119.2(5)	117.2(8)	18	2
"	1.776(8)	1.651(8)	1.34(1)	1.47(1)	1.42(1)	120.6(5)	116.7(8)	18	2
"	1.774(8)	1.663(8)	1.32(1)	1.46(1)	1.48(1)	119.9(5)	115.7(7)	18	2
"	1.752(8)	1.670(8)	1.34(1)	1.47(1)	1.47(1)	120.7(5)	115.4(7)	18	2
"	1.766(9)	1.661(9)	1.33(1)	1.42(1)	1.44(2)	120.3(5)	115.3(8)	18	2
Sn(S ₂ CNR ₂) ₄	1.73(1)	1.71(1)	1.36(2)	1.50(2)	1.49(2)	118.6(8)	116.1(-)	19	2
"	1.72(2)	1.69(2)	1.35(2)	1.50(3)	1.44(2)	118.5(10)	116.6(-)	19	2
"	1.74(2)	1.69(2)	1.30(2)	1.53(2)	1.52(2)	120.7(11)	114.6(-)	19	1
"	1.71(2)	1.67(2)	1.40(2)	1.43(3)	1.50(3)	123.6(10)	113.5(-)	19	1
Zn(S ₂ CNR ₂) ₂	1.748(19)	1.701(19)	1.325(25)	1.479(29)	1.464(30)	117.3(1.1)	117.7(1.8)	20	2
"	1.739(20)	1.699(21)	1.368(26)	1.458(34)	1.487(26)	120.2(1.2)	116.1(1.8)	20	2
TlS ₂ CNR ₂ [*]	1.74(3)	1.69(3)	1.36(3)	1.44(5)	1.44(6)	121(2)	114(3)	21	4
Tl(S ₂ CNR ₂) ₃ · H ₂ O [*]	1.69(4)	1.65(4)	1.41(5)	1.48(6)	1.52(6)	124(2)	114(3)	22	2
"	1.74(4)	1.71(4)	1.35(4)	1.50(5)	1.48(5)	121(2)	120(3)	22	2
"	1.77(5)	1.72(5)	1.35(4)	1.50(6)	1.54(6)	118(2)	123(3)	22	2
Pb(S ₂ CNR ₂) ₂	1.736(15)	1.707(15)	1.32(2)	1.46(2)	1.47(2)	119.1(9)	117.1(14)	23	2

$[\text{NEt}]_4[\text{Zn}(\text{S}_2\text{CNR}_2)_3]$	1.732(8)	1.677(8)	1.356(10)	1.468(11)	1.439(11)	122.1(5)	116.9(7)	24	1
"	1.729(7)	1.708(7)	1.318(9)	1.469(12)	1.458(11)	116.8(4)	115.1(7)	24	2
"	1.720(8)	1.681(8)	1.346(10)	1.454(12)	1.453(12)	120.8(4)	114.3(7)	24	1
TYPE 3									
$[\text{Rh}_2(\text{S}_2\text{CNR}_2)_5]\text{BF}_4 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ **	1.771(10)	1.697(11)	1.320(13)	1.449(14)	1.476(14)			25	3
"	1.761(10)	1.688(10)	1.314(13)	1.427(14)	1.494(14)			25	3
"	1.714(10)	1.709(9)	1.323(13)	1.480(15)	1.456(14)			25	2
"	1.711(10)	1.702(10)	1.332(13)	1.496(15)	1.495(16)			25	2
"	1.714(9)	1.704(9)	1.300(11)	1.503(11)	1.468(12)			25	2
$\text{Ta}(\text{S}_2\text{CNR}_2)_4 \cdot \text{Cl} \cdot \text{CH}_2\text{Cl}_2$	1.728(9)	1.722(9)	1.30(1)	1.49(1)	1.48(1)	110.8(6)	116.0(9)	26	2
"	1.732(12)	1.706(11)	1.31(1)	1.49(2)	1.46(2)	111.7(6)	117.1(11)	26	2
$[\text{Ta}(\text{S}_2\text{CNR}_2)_4]\{\text{TaCl}_6\} \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ *	1.76(3)	1.70(2)	1.30(3)	1.45(3)	1.52(4)	111(1)	118(2)	26	2
"	1.71(3)	1.66(2)	1.39(2)	1.56(3)	1.46(2)	115(1)	121(2)	26	2
"	1.74(3)	1.70(3)	1.39(4)	1.48(4)	1.48(4)	113(1)	129(2)	26	2
"	1.76(3)	1.72(2)	1.28(2)	1.48(4)	1.50(4)	109(1)	117(2)	26	2
$\text{Fe}(\text{S}_2\text{CNR}_2)_3$, 295 K	1.728(7)	1.706(8)	1.312(9)	1.481(13)	1.504(13)	113.5(4)	118.8(7)	27	2
"	1.712(6)	1.710(6)	1.328(8)	1.481(9)	1.482(9)	114.5(3)	117.8(6)	27	2
"	1.726(6)	1.697(6)	1.307(8)	1.472(11)	1.471(10)	113.6(4)	116.5(6)	27	2
"	1.718(7)	1.708(7)	1.321(10)	1.474(11)	1.504(12)	112.3(4)	118.3(7)	27	2
"	1.724(7)	1.708(7)	1.319(9)	1.476(9)	1.470(9)	112.2(4)	117.0(6)	27	2
"	1.717(7)	1.699(6)	1.325(8)	1.482(10)	1.467(10)	112.3(4)	116.6(6)	27	2
"	1.715(12)	1.701(12)	1.303(15)	1.449(20)	1.420(22)	114.1(6)	114.0(1.2)	28	2
"	1.727(10)	1.707(10)	1.307(12)	1.455(14)	1.438(14)	114.5(5)	116.1(8)	28	2
"	1.707(10)	1.699(10)	1.302(14)	1.464(16)	1.446(16)	115.5(6)	115.0(9)	28	2
"	1.724(7)	1.716(8)	1.301(10)	1.468(11)	1.467(10)	110.8(4)	115.5(7)	28	2
"	1.724(7)	1.713(7)	1.313(9)	1.466(10)	1.459(11)	110.7(4)	116.1(6)	28	2
"	1.723(8)	1.716(8)	1.328(12)	1.449(11)	1.461(10)	110.4(5)	116.4(7)	28	2

Co(S ₂ CNR ₂) ₃	1.709(5)	1.708(5)	1.315(7)	1.453(8)	1.459(8)	110.2(3)	117.5(5)	29	2
"	1.702(5)	1.703(5)	1.327(6)	1.452(8)	1.451(8)	110.4(3)	116.8(5)	29	2
"	1.703(5)	1.705(5)	1.319(6)	1.439(8)	1.448(8)	110.5(3)	117.3(5)	29	2
Cu(S ₂ CNR ₂) ₂	1.726(9)	1.716(8)	1.31(1)	1.45(2)	1.45(2)	113.4(5)	115.3(9)	30	2
Ni(S ₂ CNR ₂) ₂	1.750(8)	1.691(8)	1.349(9)	1.453(10)	1.473(10)	109.9(4)	118.4(5)	31	2

Compound

S(1)–C(1)	S(2)–C(1)	C(1)–N	N–C(2)	N–C(3)	S–C–S	C–N–C	Ref.
TYPE 1							
NaS ₂ CNR ₂ ·3H ₂ O	1.729(6)	1.712(7)	1.344(8)	1.479(8)	1.475(9)	114.3(5)	32
LiS ₂ CNR ₂ ·3H ₂ O	1.724(1)	1.722(1)	1.337(2)	1.466(2)	1.472(2)	114.0(1)	33
[(CH ₃ CH ₂) ₂ NH ₂][S ₂ CNR ₂]	1.731(2)	1.699(2)	1.349(3)	1.462(3)	1.465(3)	115.2(2)	34
TYPE 2							
Pb(S ₂ CNR ₂) ₂ [*]	1.724(24)	1.709(37)	1.378(48)	1.501(71)	1.488(48)	121.0(1.9)	35
"	1.745(27)	1.635(27)	1.362(34)	1.481(36)	1.495(43)	121.4(1.6)	35
Te(S ₂ CNR ₂) ₂	1.74(2)	1.69(2)	1.36(2)	1.43(2)	1.47(3)	117.9(9)	36
"	1.73(2)	1.71(2)	1.33(2)	1.48(3)	1.50(2)	118.6(7)	36
Sb(S ₂ CNR ₂) ₃	1.73(1)	1.71(1)	1.36(2)	1.50(2)	1.48(2)	118.9(8)	37
"	1.77(1)	1.69(1)	1.33(2)	1.47(2)	1.47(2)	118.2(8)	37
"	1.73(1)	1.70(1)	1.34(2)	1.46(2)	1.52(2)	118.7(7)	37
Bi(S ₂ CNR ₂) ₃	1.75(2)	1.71(2)	1.30(2)	1.52(2)	1.51(2)	118.5(9)	37
"	1.77(2)	1.67(2)	1.35(2)	1.44(2)	1.51(2)	120.4(1.0)	37
"	1.76(2)	1.73(2)	1.31(2)	1.47(3)	1.49(2)	116.6(1.1)	37
Hg ₂ (S ₂ CNR ₂) ₄	1.735(20)	1.715(19)	1.33(2)	1.54(3)	1.52(3)	119.2(9)	38
"	1.764(19)	1.698(21)	1.33(2)	1.43(3)	1.49(3)	120.2(1.0)	38
Hg(S ₂ CNR ₂) ₂	1.782(12)	1.691(12)	1.29(2)	1.51(2)	1.46(2)	117.9(5)	38
Te(S ₂ CNR ₂) ₄	1.74(2)	1.73(2)	1.32(2)	1.46(2)	1.49(2)	114.9(7)	39
"	1.73(2)	1.70(2)	1.32(2)	1.45(2)	1.55(2)	117.7(8)	39
"	1.75(2)	1.67(2)	1.33(2)	1.44(2)	1.50(2)	118.1(1.0)	39
"	1.70(2)	1.70(2)	1.37(2)	1.52(2)	1.49(2)	119.5(8)	39
"	1.71(2)	1.68(2)	1.34(2)	1.53(2)	1.51(2)	118.6(8)	39
Zn(S ₂ CNR ₂) ₂	1.737(9)	1.723(10)	1.310(12)	1.480(15)	1.480(14)	115.7(1.2)	51

$Zn(S_2CNR_2)_2$	1.725(10)	1.722(10)	1.340(13)	1.440(14)	1.450(15)	117.5(9)	116.4(1.2)	51
$Te(S_2CNR_2)_4$	1.70(2)	1.69(2)	1.37(2)	1.53(2)	1.47(2)	119.4(8)	119.0(1.3)	39
"	1.76(2)	1.65(2)	1.40(2)	1.52(2)	1.53(2)	121.0(9)	115.0(1.2)	35
"	1.73(2)	1.72(2)	1.33(2)	1.46(2)	1.51(2)	117.6(7)	114.7(1.1)	39
$Se(S_2CNR_2)_2$	1.77(2)	1.66(2)	1.33(2)	1.50(2)	1.54(2)	117.6(9)	113.6(1.9)	40
"	1.75(2)	1.65(2)	1.38(2)	1.50(2)	1.49(2)	120.1(8)	118.1(1.1)	40
$Tl(S_2CNR_2)_3$	1.713(7)	1.713(7)	1.36(2)	1.47(2)	1.47(2)	120.2(7)	118(1)	41
"	1.733(11)	1.709(8)	1.32(1)	1.49(2)	1.49(1)	119.9(6)	115(1)	41
AgS_2CNR_2	1.734(9)	1.710(12)	1.340(14)	1.501(19)	1.476(12)	121.3(6)	116.1(10)	42
"	1.738(7)	1.727(10)	1.328(14)	1.471(16)	1.482(10)	122.2(6)	113.7(9)	42
"	1.760(10)	1.721(12)	1.315(9)	1.465(18)	1.503(14)	120.9(4)	115.1(7)	42
$Th(S_2CNR_2)_4^*$	1.78(5)	1.66(6)	1.35(6)	1.42(6)	1.51(7)	118.5(2.9)	113.9(3.9)	43
"	1.73(5)	1.73(5)	1.27(6)	1.64(6)	1.50(8)	118.6(2.7)	113.0(3.7)	43
$Ga(S_2CNR_2)_3$	1.716(4)	1.716(4)	1.324(9)	1.465(9)	1.465(9)	115.9(4)	116.3(6)	44
"	1.730(6)	1.714(4)	1.325(7)	1.483(9)	1.461(6)	116.5(3)	116.3(5)	44
$In(S_2CNR_2)_3$	1.723(3)	1.723(3)	1.329(7)	1.468(8)	1.468(8)	118.3(3)	117.0(5)	44
"	1.736(5)	1.719(4)	1.326(6)	1.476(7)	1.476(6)	118.4(3)	115.8(4)	44
$As(S_2CNR_2)_3$	1.76(1)	1.67(1)	1.34(2)	1.46(2)	1.47(2)	119.3(7)	114(1)	45
"	1.77(1)	1.68(1)	1.31(2)	1.49(2)	1.45(2)	118.5(9)	115(1)	45
"	1.75(1)	1.71(1)	1.34(2)	1.47(2)	1.47(2)	118.6(8)	119(1)	45
$Sn(S_2CNR_2)_2$	1.718(9)	1.682(9)	1.370(12)	1.457(12)	1.511(12)	120.5(4)	114.9(6)	46
"	1.725(9)	1.723(9)	1.346(12)	1.494(12)	1.482(12)	118.8(4)	115.5(6)	46
$Sn(S_2CNR_2)_4^*$	1.76(2)	1.67(2)	1.34(4)	1.52(4)	1.51(4)	121(2)	112(2)	47
"	1.75(2)	1.71(2)	1.31(4)	1.49(4)	1.48(4)	116(2)	115(2)	47
$Cd(S_2CNR_2)_2$	1.725(14)	1.714(14)	1.33(2)	1.49(2)	1.50(2)	120.2(7)	116.6(1.1)	48
"	1.741(15)	1.734(14)	1.32(2)	1.52(2)	1.46(2)	117.5(7)	116.6(1.1)	48
$Hg(S_2CNR_2)_2$	1.76(2)	1.69(2)	1.32(3)	1.43(5)	1.57(3)	120(1)	112(2)	49
TlS_2CNR_2	1.72(1)	1.71(1)	1.32(1)	1.51(2)	1.48(2)	118.6(4)	115.3(9)	50
"	1.72(1)	1.70(1)	1.35(1)	1.49(2)	1.50(2)	119.5(3)	114.6(9)	50

TYPE 3

$\text{Mo}(\text{S}_2\text{CNR}_2)_4$	1.69(1)	1.69(1)	1.33(2)	1.53(2)	1.51(2)	111.7(6)	118(1)	52	2
"	1.72(1)	1.70(1)	1.34(2)	1.50(2)	1.46(2)	110.6(6)	119(1)	52	2
$\text{W}(\text{S}_2\text{CNR}_2)_4 \cdot \text{Br}^*$	1.74(3)	1.66(3)	1.34(3)	1.71(4)	1.51(4)	110(1)	118(2)	53	2
"	1.71(2)	1.64(2)	1.33(3)	1.55(3)	1.59(3)	113(1)	118(2)	53	2
"	1.71(3)	1.71(3)	1.34(3)	1.49(3)	1.50(3)	110(1)	116(2)	53	2
"	1.74(2)	1.72(2)	1.29(3)	1.47(3)	1.51(3)	109(1)	120(2)	53	2
$\text{Os}_2(\text{S}_2\text{CNR}_2)_6(\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$	1.73(1)	1.71(1)	1.32(2)	1.53(2)	1.50(2)	110.4(6)	118(1)	54	2
"	1.70(1)	1.68(1)	1.30(2)	1.53(2)	1.58(2)	109.0(8)	116(1)	54	2
"	1.73(1)	1.66(1)	1.34(2)	1.51(2)	1.52(2)	112.0(7)	118(1)	54	2
"	1.71(1)	1.68(1)	1.32(2)	1.52(2)	1.53(2)	109.4(7)	118(1)	54	2
"	1.76(1)	1.71(1)	1.30(1)	1.47(2)	1.51(2)	106.9(6)	116(1)	54	3
"	1.77(1)	1.67(1)	1.32(1)	1.47(2)	1.51(2)	108.2(6)	117(1)	54	3
$\text{Mn}(\text{S}_2\text{CNR}_2)_3^*$	1.74(2)	1.69(2)	1.34(3)	1.54(3)	1.52(3)	118(1)	114(2)	55	2
"	1.77(2)	1.65(3)	1.40(3)	1.48(3)	1.54(3)	115(1)	120(2)	55	2
"	1.75(3)	1.67(2)	1.33(3)	1.49(3)	1.57(4)	116(1)	117(2)	55	2
$\text{Rh}(\text{S}_2\text{CNR}_2)_3^*$	1.71(2)	1.69(2)	1.36(2)	1.50(3)	1.50(3)	113(1)	119(1)	45	2
"	1.74(2)	1.73(2)	1.32(3)	1.46(3)	1.51(3)	110(1)	121(2)	45	2
"	1.73(2)	1.70(2)	1.37(3)	1.49(3)	1.51(3)	111(1)	120(2)	45	2
$\text{Ti}(\text{S}_2\text{CNR}_2)_4$ (Average ligand)	1.72(2)	1.68(2)	1.34(3)	1.50(3)	1.52(3)	113(1)	118(2)	56	2
$\text{Ru}(\text{S}_2\text{CNR}_2)_3$	1.72(1)	1.71(1)	1.27(2)	1.51(2)	1.51(3)	110.6(8)	114.0(1.3)	57	2
"	1.73(1)	1.71(1)	1.32(2)	1.49(2)	1.50(2)	110.3(8)	118.2(1.2)	57	2
"	1.72(1)	1.71(1)	1.30(2)	1.61(3)	1.48(2)	111.3(9)	113.1(1.4)	57	2
$\text{Au}(\text{S}_2\text{CNR}_2)_3^*$	1.75(2)	1.74(2)	1.28(2)	1.48(2)	1.46(2)	110.2(8)	118(2)	58	2
"	1.76(2)	1.66(2)	1.32(2)	1.47(2)	1.45(2)	120(1)	115(2)	58	1
"	1.78(2)	1.66(2)	1.34(2)	1.50(2)	1.48(2)	120(1)	115(2)	58	1

$[\text{Mo}(\text{S}_2\text{CNR}_2)_4][\text{Mo}_6\text{O}_{19}]$	1.72(2)	1.67(2)	1.31(2)	1.46(2)	1.49(2)	110.8(8)	115.9(1.2)	59	2
"	1.74(2)	1.68(2)	1.32(2)	1.47(3)	1.48(2)	110.8(3)	119.4(1.4)	59	2
"	1.74(1)	1.71(2)	1.29(2)	1.50(2)	1.47(2)	109.7(7)	118.1(1.2)	59	2
"	1.74(2)	1.68(2)	1.32(2)	1.49(2)	1.45(2)	110.5(8)	120.3(1.3)	59	2
$\text{Mo}(\text{S}_2\text{CNR}_2)_4 \cdot \text{Cl}$	1.72(1)	1.70(2)	1.29(2)	1.54(2)	1.46(2)	110.2(8)	117.3(1.3)	59	2
"	1.72(1)	1.70(1)	1.32(2)	1.48(2)	1.47(2)	110.2(7)	116.1(1.2)	59	2
"	1.72(2)	1.68(2)	1.33(2)	1.48(2)	1.45(2)	111.0(8)	119.3(1.3)	59	2
"	1.71(2)	1.70(2)	1.29(2)	1.47(2)	1.59(3)	110.3(9)	117(1.6)	59	2
$\text{Ir}(\text{S}_2\text{CNR}_2)_3$	1.715(7)	1.715(7)	1.33(1)	1.48(2)	1.48(2)	110.5(6)	117.7(9)	60	2
"	1.720(8)	1.714(8)	1.326(9)	1.46(1)	1.48(1)	110.9(4)	117.4(7)	60	2
$\text{Co}(\text{S}_2\text{CNR}_2)_3$	1.714(8)	1.714(8)	1.304(15)	1.492(16)	1.492(16)	109.6(7)	120.8(1.2)	61	2
"	1.703(7)	1.695(9)	1.327(10)	1.502(10)	1.486(14)	110.3(4)	119.5(7)	61	2
$\text{Ni}(\text{S}_2\text{CNR}_2)_2$	1.713(7)	1.700(7)	1.330(10)	1.490(13)	1.480(17)	110.6(6)	116.9(1.2)	62	2
$\text{Cu}(\text{S}_2\text{CNR}_2)_2$	1.713(8)	1.711(8)	1.350(10)	1.470(12)	1.470(11)	114.6(7)	117.5(1.0)	63	2
"	1.736(7)	1.708(7)	1.330(8)	1.460(10)	1.460(10)	112.9(6)	116.9(8)	63	2
$\text{Cr}(\text{S}_2\text{CNR}_2)_3$	1.723(8)	1.716(8)	1.315(9)	1.44(1)	1.52(1)	114.3(4)	116.8(6)	64	2
"	1.720(7)	1.720(7)	1.341(8)	1.49(1)	1.46(1)	113.6(3)	118.8(5)	64	2
"	1.728(8)	1.711(8)	1.323(8)	1.60(2)	1.48(1)	114.1(4)	117.1(6)	64	2
$\text{Fe}(\text{S}_2\text{CNR}_2)_3$	1.711(10)	1.704(9)	1.349(10)	1.532(13)	1.462(13)	112.7(4)	119.6(8)	65	2
"	1.720(10)	1.710(10)	1.320(10)	1.514(11)	1.503(12)	112.0(5)	118.7(9)	65	2
"	1.705(10)	1.700(9)	1.343(10)	1.485(11)	1.481(12)	113.4(4)	120.4(9)	65	2
"	1.720(4)	1.720(4)	1.326(6)	1.480(7)	1.480(7)	111.3(2)	117.4(4)	65	2
"	1.723(4)	1.720(4)	1.320(6)	1.466(7)	1.493(8)	110.9(2)	118.8(5)	65	2
$\text{Fe}(\text{S}_2\text{CNR}_2)_2$	1.734(5)	1.731(5)	1.330(6)	1.489(6)	1.492(7)	115.7(3)	116.1(4)	66	2
"	1.766(5)	1.721(5)	1.321(5)	1.480(6)	1.492(7)	114.7(3)	115.2(4)	66	3
$\text{CuS}_2\text{CNR}_2^*$	1.721(27)	1.695(25)	1.408(33)	1.501(37)	1.464(32)	125.5(1.7)	114.8(2.4)	67	3
$\text{Mn}(\text{S}_2\text{CNR}_2)_2$	1.74(1)	1.71(1)	1.34(2)	1.50(2)	1.49(2)	118.6(8)	117.2(1.1)	68	3
"	1.73(1)	1.70(2)	1.34(2)	1.49(2)	1.50(2)	119.2(7)	114.0(1.1)	68	3

$\text{Fe}(\text{S}_{\text{2}}^{\text{CNR}})_3 \cdot \text{I}_5$	1.724(13)	1.696(15)	1.295(15)	1.50(2)	1.46(2)	110.2(7)	116.7(1.1)	69	2
"	1.723(13)	1.717(11)	1.292(14)	1.46(2)	1.48(2)	109.4(6)	117.1(9)	69	2
"	1.734(11)	1.689(15)	1.291(16)	1.50(2)	1.64(2)	109.3(6)	119.2(1.2)	69	2

R_2 = Diisopropyl

Compound	S(1)-C(1)	S(2)-C(1)	C(1)-N	N-C(2)	N-C(3)	S-C-S	C-N-C	Ref.	P
TYPE 1									
$\text{NaS}_2\text{CNR}_2 \cdot 5\text{H}_2\text{O}$	1.747(6)	1.702(6)	1.348(8)	1.485(8)	1.486(8)	118.3(4)	113.8(5)	70	0
$\text{LiS}_2\text{CNR}_2 \cdot 3\text{H}_2\text{O}$	1.740(6)	1.709(6)	1.341(8)	1.508(8)	1.486(9)	117.5(3)	114.5(5)	71	0
$[\text{NH}_2\text{R}_2][\text{S}_2\text{CNR}_2]$	1.734(3)	1.701(3)	1.349(4)	1.486(4)	1.491(4)	117.7(2)	113.8(2)	72	0
TYPE 2									
$\text{Zn}(\text{S}_2\text{CNR}_2)_2$	1.756(3)	1.712(3)	1.321(4)	1.501(5)	1.492(4)	115.9(2)	114.4(2)	73	3
"	1.733(3)	1.723(3)	1.329(3)	1.491(4)	1.491(4)	115.4(1)	114.8(2)	73	2
$\text{Hg}(\text{S}_2\text{CNR}_2)_2$	1.753(12)	1.717(12)	1.311(15)	1.49(2)	1.52(2)	116.3(7)	114.8(10)	74	2
$\text{Pb}(\text{S}_2\text{CNR}_2)_2$	1.714(14)	1.717(14)	1.32(2)	1.46(3)	1.52(3)	116.7(8)	115.8(1.7)	75	2
"	1.729(14)	1.700(14)	1.33(2)	1.49(2)	1.52(2)	117.9(8)	112.6(1.2)	75	2
TYPE 3									
$[\text{Ru}_2(\text{S}_2\text{CNR}_2)_5]_2[\text{Ru}_2\text{Cl}_6] \cdot 2\text{C Cl}_3$	1.69(3)	1.67(3)	1.32(4)	1.59(4)	1.56(4)	113(2)	114(2)	76	2
"	1.71(3)	1.74(3)	1.34(4)	1.51(4)	1.56(4)	110(1)	114(2)	76	2
"	1.67(3)	1.78(4)	1.31(4)	1.49(4)	1.56(4)	109(2)	119(2)	76	3
"	1.75(3)	1.67(4)	1.39(4)	1.60(5)	1.60(4)	112(2)	120(2)	76	3
"	1.71(3)	1.71(3)	1.34(4)	1.55(4)	1.48(5)	110(2)	122(3)	76	2
$[\text{Ru}_2(\text{S}_2\text{CNR}_2)_5]\text{Cl} \cdot 2.5\text{C}_6\text{H}_6$	1.70(2)	1.70(2)	1.32(2)	1.50(2)	1.50(2)	111(1)	123(1)	76	2
"	1.70(2)	1.81(2)	1.34(2)	1.53(2)	1.52(2)	108(1)	118(1)	76	3
"	1.65(2)	1.86(2)	1.31(2)	1.53(2)	1.56(2)	106(1)	116(1)	76	3
"	1.70(2)	1.70(2)	1.35(2)	1.51(3)	1.54(3)	112(1)	119(1)	76	2
"	1.70(2)	1.71(2)	1.38(2)	1.55(3)	1.50(2)	112(1)	120(1)	76	2
$\text{Pd}[1:3,4\text{-}n\text{-C}_4(\text{tolyl})_4\text{Ph}](\text{S}_2\text{CNR}_2)_2$	1.739(10)	1.708(10)	1.331(13)	1.530(15)	1.494(14)	112.2(6)	117.1(8)	77	2

$\text{FeCl}(\text{S}_2\text{CNR}_2)_2 \cdot \text{CHCl}_3$	1.732(7)	1.724(6)	1.309(7)	1.491(8)	1.508(9)	108.4(3)	116.7(5)	78	2
"	1.728(7)	1.727(5)	1.319(8)	1.501(8)	1.501(11)	108.8(3)	115.9(3)	78	2
$\text{Cu}(\text{S}_2\text{CNR}_2)_2$	1.710(6)	1.727(7)	1.321(7)	1.490(9)	1.492(8)	111.1(3)	115.8(5)	79	2
"	1.718(7)	1.725(6)	1.328(8)	1.501(8)	1.477(9)	112.0(4)	116.0(5)	79	2
$\text{Ni}(\text{S}_2\text{CNR}_2)_2$	1.711(11)	1.714(12)	1.329(15)	1.48(2)	1.49(2)	109.2(6)	117.3(1.0)	80	2
"	1.673(12)	1.720(12)	1.337(17)	1.55(3)	1.50(3)	109.5(7)	117.4(1.4)	80	2

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